



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
 17.05.2000 Bulletin 2000/20

(51) Int. Cl.⁷: **H01L 21/311**, H01L 21/02,
 H01L 29/51, H01L 21/8242,
 H01L 27/115, H01L 29/92

(21) Application number: 99202911.6

(22) Date of filing: 09.09.1999

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
 Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 09.09.1998 US 99571 P
 11.09.1998 US 99848 P
 30.12.1998 US 114228 P
 10.03.1999 US 123687 P

(71) Applicant:
 Texas Instruments Incorporated
 Dallas, Texas 75251 (US)

(72) Inventors:
 • Molse, Theodore S.
 Dallas, Texas 75238 (US)
 • Xing, Guoqiang
 Plano, Texas 75093 (US)

• Visokay, Mark
 Rowlett, Texas 75088 (US)
 • Gaynor, Justin F.
 Dallas, Texas 75214 (US)
 • Summerfelt, Scott R.
 Garland, Texas 75094 (US)
 • Gilbert, Stephen R.
 Dallas, Texas 75204 (US)
 • Celli, Francis
 Dallas, Texas 75248 (US)
 • Colombo, Luigi
 Dallas, Texas 75248 (US)
 • Kressley, Mark A.
 Richardson, Texas 75081 (US)

(74) Representative: Holt, Michael
 Texas Instruments Limited,
 European Patents Department (MS 13),
 PO Box 5069
 Northampton NN4 7ZE (GB)

(54) **Integrated circuit comprising a capacitor and method**

(57) A via etch to contact a capacitor with ferroelectric between electrodes together with dielectric on an insulating diffusion barrier includes two-step etch with

F-based dielectric etch and Cl- and F-based barrier etch.

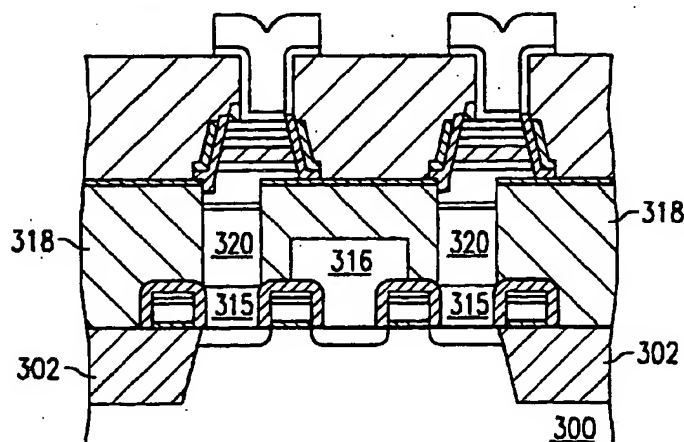


FIG. 6f

Description

BACKGROUND OF THE INVENTION

- 5 [0001] The invention relates to electronic semiconductor devices, and, more particularly, to capacitor and memory structures and fabrication methods for such structures.
- [0002] High density integrated circuit memories have density dominated by cell size; thus alternative capacitor dielectrics such as high dielectric constant paraelectric for dynamic memory (DRAM) and ferroelectrics for nonvolatile ferroelectric memory (FeRAM) have recently received intense investigation. The paraelectric currently being investigated include barium strontium titanate (BST) and tantalum pentoxide (Ta₂O₅) and the ferroelectrics include strontium bismuth tantalate (SBT) and lead zirconate titanate (PZT). See for example, Hintermaier et al, Properties of SrBi₂Ta₂O₅ Thin Films Grown by MOCVD for High Density FeRAM, 1998 Symp. VLSI Tech. Dig. 56.
- 10 [0003] However, memories with these new dielectrics have manufacturing problems.

15 SUMMARY OF THE INVENTION

- [0004] The present invention provides fabrication for paraelectric and ferroelectric capacitors, and includes multi-step stack etches with remote endpoint detection for step transitions.
- [0005] This has the advantages of manufacturability for paraelectric and ferroelectric capacitors with metal oxide dielectrics such as PZT, BST, and SBT.
- 20

BRIEF DESCRIPTION OF THE DRAWINGS

- [0006] The present invention will now be further described, by way of example, with reference to certain exemplary embodiments illustrated in the accompanying drawings in which:
- 25

Figures 1a-1b illustrates an ECR reactor and RF current and voltage sensor.

Figure 2 schematically shows the functional parts of a DRAM.

Figures 3a-3o show in cross sectional elevation views preferred embodiment fabrication method.

30 Figures 4a-4h illustrate an alternative structure.

Figures 5a-5b show etch parameters.

Figures 6a-6f are cross sectional elevation views of another preferred embodiment fabrication method.

Figures 7a-7d illustrate sidewall geometry and endpoint detection.

Figure 8 shows a third preferred embodiment step.

35 Figures 9a-9f illustrate remote endpoint detection in a stack etch.

Figures 10a-10c show a capacitor under bitline preferred embodiment.

Figures 11a-11f show nucleation of ferroelectric.

Figures 12a-12h illustrate seed layer for ferroelectric deposition.

Figures 13a-13i are cross sectional elevation views of a three dimensional capacitor fabrication.

40 Figure 14 shows alternative via etching.

Figure 15 illustrates etch selectivity.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

- 45 [0007] The preferred embodiments provide fabrication methods and structures for ferroelectric and high-dielectric-constant paraelectric integrated circuit capacitors and random access memories including multi-step stack etches of electrodes and dielectric within a single plasma reactor using remote endpoint detection for etch step transitions.
- [0008] Figures 1a-1b illustrates an ECR reactor setup for use with the preferred embodiments, although other reactors could be used. Figure 2 schematically shows the functional blocks of a DRAM. An FeRAM is analogous but with drive lines (paralleling the word lines) replacing the common capacitor plate.
- 50 [0009] Figure 3a-o illustrates in cross sectional elevation views the steps of first preferred embodiment fabrication methods for integrated circuits (e.g., CMOS or BiCMOS) with capacitors or memory cells (e.g., DRAM or FeRAM cells) as follows.

- 55 (1) Start with a silicon wafer (or silicon on insulator wafer) with shallow trench isolation and twin wells for CMOS devices. Perform threshold adjustment implants (which may differ for cell transistors and various peripheral transistors), and form gate dielectric. Deposit tungsten silicide coated polysilicon gate material and a silicon dioxide layer, then pattern the layers to form oxide-topped gates plus gate level interconnects. The gate material could also pro-

vide a polysilicon emitter for bipolar devices which would also require a prior base implant. See Figure 3a which shows silicon substrate 300 with shallow trench isolation oxide 302 plus gate dielectric 304, gates 306, and gate level interconnect 307 (i.e., wordlines for a memory array). Gates 306 may be 200-300 nm high and 100-250 nm long (Figure 3a is a cross section along the gate length, and gates typically have widths much greater than their lengths). An alternative would be formation of polysilicon gates followed by a self-aligned silicidation (after the source/drain and sidewall dielectric formations of the next step) to create a silicide on both the gate top and the source/drains.

(2) Perform lightly doped drain implants, and then form sidewall dielectric 308 on the gates by deposition plus anisotropic etching. Introduce dopants to form sources and drains 310-312. Cover the gate level structure with a planarized dielectric layer 314 (such as BPSG or a stack of conformal and planarized layers including undoped oxide such as a deposition from TEOS); see Figure 3b.

(3) Photolithographically define and etch holes (contacts, vias) in planarized dielectric 314 down to selected sources 312 for eventual DRAM cell stems. Blanket deposit in-situ-doped polysilicon and etch back to form stems 315 filling the vias.

(4) Photolithographically define and etch holes (contacts, vias) in planarized dielectric 314 down to selected drains 310 for eventual bitline contacts. Blanket deposit in-situ-doped polysilicon and a tungsten silicide cap; and then photolithographically define and etch to form bitlines 316. Deposit oxide to form above-bitline dielectric 318 on the bitlines plus remaining dielectric 314 (which for convenience is no longer separately designated); see Figure 3c.

(5) Photolithographically define and etch openings (holes, vias) in dielectric 318 down to the tops of stems 315 and fill by blanket deposit in-situ-doped polysilicon and etchback to form stem extensions 320; see Figure 3d. The etch-back may recess stems 320 about 20 to 50 nm below the surface of 318.

(6) Blanket deposit titanium metal to a thickness of about 20 nm and then react in a nitrogen atmosphere with exposed polysilicon stems 320 to form titanium silicide 321 on the tops of stems 320 and in recessed in dielectric 318. Strip the unreacted titanium and titanium nitride which forms over dielectric 318.

(7) Sputter deposit 50 nm thick TiAlN with a composition having a Ti to Al ratio of about 3 to 1 and approximately stoichiometric with respect to nitrogen, although sputtering Ti and Al through a nitrogen plasma typically yields a nitrogen deficient compound. Then apply CMP to planarized plus remove all TiAlN except for TiAlN 322 on silicide 321; TiAlN 322 forms a conductive diffusion barrier and keeps oxygen away polysilicon to prevent silicon dioxide formation by diffusing oxygen or silicon. See Figure 3e.

[23341] Alternatively, instead of the openings being filled with polysilicon 320 in step (5), the openings could be filled with TiN (or other conductive barrier materials) deposited by CVD and planarized. Indeed, even polysilicon 315 could be replaced by TiN. In particular, the blanket deposition of titanium metal would be the same as in the foregoing, and the reaction to form TiSi_2 on the opening bottom (whether on polysilicon 315 or on source 312) would also be the same. Then deposit TiN by CVD sufficient to fill the opening (e.g., 150 nm thick). The deposition could be with from a mixture of ammonia plus a precursor such as TiCl_4 or TDMAT ($\text{Ti}[\text{N}(\text{CH}_3)_2]_4$) or TDEAT ($\text{Ti}[\text{N}(\text{C}_2\text{H}_5)_2]_4$). TiN formed from TiCl_4 has shown 100% step coverage for aspect ratios of the openings as high as 13 to 1 and exhibits a film resistivity of less than 100 uohm-cm. TiN films formed from TDMAT or TDEAT can be either conformal or low resistivity but cannot be both. The advantage of organic precursors is their low growth temperature (300-400 C). However, the resistivity of organic CVD TiN is higher (200-10000 ohm-cm) than TiCl_4 precursor due to the carbon content. The major problem of TiCl_4 grown TiN is the Cl residue in the TiN films; this can cause corrosion of Al used for overlying metal. Cl content of less than 1% has been obtained and reasonable reliability has been achieved when the TiN is in contact with Al. Of course, the use of W metallization avoids the Cl problem.

After the TiN deposition, planarize CMP as in the foregoing.

The bulk resistance of the TiN filled opening (presume the opening has a diameter of 0.2 μm and a depth of 1 μm) will be about 30 ohm when filled with TiN grown by TiCl_4 CVD at 400 C. Because the resistivity of TiN formed from TiCl_4 decreases as the growth temperature increases, the resistance will drop to 22 ohms if the TiN is grown at 650 C. Growing TiN at higher temperatures also reduces the content of Cl. Given the fact that the contact resistance of a TiN/ TiSi_2 /Si stack of 0.25 μm diameter is roughly 250 ohm for n+ Si and 1000 ohm for p+ Si, the resistance contribution from the bulk of TiN in the opening will be small. Indeed, organic grown TiN with resistivities of 2000 uohm-cm can be used to fill the opening with a bulk resistance of roughly 600 ohm; this is comparable to the contact resistance.

(8) Sputter deposit thin (3 nm) adhesion layer 324 of TiAlN; this provides for Pt adhesion to dielectric 318.

(9) Sputter deposit 200-400 nm thick layer 326 of Pt; see Figure 3f. This thickness determines the height of the resulting pillar capacitor and thus the capacitance, so circuit requirements determine the height.

(10) Sputter deposit 50 nm thick hardmask TiAlN (roughly $\text{Ti}_{0.75}\text{Al}_{0.25}\text{N}$) layer 328, a thin hardmask implies less sidewall for redeposition of Pt during Pt etching. An alternative is a hardmask of other Ti to Al ratios or TiN or TiSiN or TiAlSiN .

(11) [Ti-27124] Treat TiAlN hardmask layer 328 with oxygen to increase subsequent etch selectivity and limit pitting of the eventual Pt electrode. In effect, some Al and Ti will oxidize to form AlO_x (e.g., Al_2O_3) and TiO_x (e.g., TiO_2) at and near the surface of the hardmask, and this surface will better withstand the low pressure (effectively sputtering) chlorine etch of Pt 326. The preferred treatment for TiAlN hardmask 332 is a 2 minute exposure to a plasma of N_2 and N_2O (flows of 2200 and 1800 sccm, respectively) at a pressure of roughly 20 Torr and a power of 500 W at 450 C for an 8 inch wafer. Note that the TiAlN likely is nitrogen deficient, and the N_2O and N_2 also help maintain the nitrogen content. This treatment reduces the etch rate of the hardmask during the Pt etch by a factor of roughly 5.

Alternative oxygen treatments of TiAlN hardmask layer 328 include an anneal in O_2 with a pressure of 10 Torr at a temperature of 700 C for 2 minutes. This high temperature anneal is somewhat more effective than the N_2O plasma and further reduces the hardmask etch rate. Lower temperature O_2 anneals likewise reduce the etch rate but not as significantly. In particular, a 2 minute O_2 anneal at 600 C is less effective than the N_2O and N_2 plasma treatment, and a 450 C anneal even less.

Further, an oxygen plasma such as used for photoresist ash can also provide an oxygen treatment for the TiAlN hardmask and reduce the etch rate, but this is less effective than the N_2O and N_2 plasma treatment.

For the alternative hardmask of TiN, the same oxygen treatments (N_2O and O_2 plasmas or O_2 anneal) can be used, and lower temperatures anneals are effective. In fact, a 450 C anneal in O_2 for a TiN hardmask reduces the hardmask etch rate by about the same factor as a 600-700 C anneal for the TiAlN hardmask. Thus increasing the Al content requires increasing the oxidation conditions because the TiAlN is more oxidation resistant than TiN.

(12) [x26191] Deposit by PECVD with silane and N_2O layer 329 of SiON to act as an antireflective coating (ARC). This can use the same N_2O plasma chamber as used in the oxygen treatment of the TiAlN in the preceding step. The thickness and composition of layer 329 are adjusted to effectively eliminate reflections at the photoresist-ARC interface by use of destructive wave interference. For example, use a composition of roughly $\text{Si}_{0.46}\text{O}_{0.45}\text{N}_{0.09}$ with a thickness of 25 nm for 248 nm wavelength exposure of photoresist.

An alternative is to use organic ARC which just absorbs the exposure radiation. An ARC thickness of 60 nm typically suffices.

(13) Spin on photoresist. Expose and develop the photoresist to define the locations of the bottom electrodes; see Figure 3g with resulting patterned photoresist 330. The bottom electrodes may have a rectangular footprint of 1f by 2f-3f, with f the feature size (100-250 nm), depending upon capacitance requirements.

(14) Use the patterned photoresist 330 as a mask to etch ARC 329 with a fluorine based plasma (e.g., CF_4 + CHF_3) and then to etch TiAlN 328 with a chlorine-based plasma (e.g., Cl_2). Alternatively, an argon-chlorine plasma (Ar/Cl_2 ratio about 0.2 to 1.5) with a small amount (5-20%) of CHF_3 can be used to etch both SiON ARC 329 and TiAlN 328. Next, strip photoresist 330 with an oxygen plasma, and optionally also strip the exposed ARC with a fluorine based plasma, although the ARC can remain and act as additional hardmask. (In the case of organic ARC, then a strip is preferred to limit production of residue during the Pt etch.) This leaves TiAlN hardmask 332 on Pt layer 326; see Figure 3h. The TiAlN etch could be in an ECR single wafer plasma etcher with a gas of Cl_2 at a pressure of 10 mTorr and a low plasma bias (< 200 V); this etches TiAlN about 10 faster than it etches Pt.

An alternative applies the oxygen treatment to the TiAlN hardmask of foregoing step (11) after this patterning of the TiAlN.

(15) [26778+26586] Use hardmask 332 with a plasma etch to etch Pt 326 and thereby form bottom electrode 334; see Figure 3i. The etch uses a low pressure (0.5-1 mTorr), high-density plasma of Cl_2 + O_2 + N_2 in a single wafer ECR plasma etcher with a plasma bias of 300 V. This provides mostly a sputtering of Pt, PtCl_x compounds have very low vapor pressure. Raising the wafer temperature to 400 C will help PtCl_x volatility. The O_2 helps keep an oxidized surface on TiAlN 332 to deter erosion by the etch, and the N_2 helps maintain the nitrogen content of TiAlN 332 and thereby also slows erosion. Further, the nitrogen apparently deters sidewall redeposition of Pt, and this results in steeper sidewall slopes. The nitrogen may form a partial monolayer on the Pt sidewall surface that effectively decreases the sticking coefficient of sputtered Pt atoms, or the nitrogen may combine with oxygen to form such a partial monolayer.

A plasma excited from the mixture of Cl_2 + O_2 + N_2 in roughly equal amounts theoretically yields a majority of Cl^+ ions with lesser portions of O^+ and other ions such as N^+ , Cl_2^+ and O_2^+ . Thus the sputter etching should primarily be Cl^+ sputtering of the Pt. Consequently, a plasma from a gas mixture of Ar + O_2 + N_2 will have roughly similar sputtering because the Ar^+ ions generated have about the same mass as Cl^+ ions; however, the use of Ar does not lead to analogs of PtCl_x type complexes, and so an Ar -alone plasma is less effective at removal of sputtered Pt. A plasma excited from an Ar + O_2 + N_2 mixture will still have the O_2 and N_2 effects of deterring TiAlN hardmask erosion plus effectively reducing sticking coefficient of redepositing Pt. A mixture of Ar + Cl_2 + O_2 + N_2 will provide intermediate results. These etches yield a sidewall slope of 70-80 degrees. Gas mixtures with other oxygen and nitrogen sources, such as N_2O , could be used along with the sputtering species Cl . At least about 5% O_2 (or other O source) appears sufficient to maintain the hardmask and over roughly 70% O_2 slows the Pt etching

rate too much. Similarly, at least about 5% N₂ (or other N source) appears sufficient to maintain the hardmask and over roughly 80% N₂ slows the Pt etching. A mixture of 25% O₂, 50% N₂, and 25% Cl₂ + Ar works well. More generally, Figure 5a illustrates preferred embodiment mixtures within the dashed lines.

[27127] Detect the endpoint of the Pt etch (i.e., when the Pt is just clearing the underlying TiAlN 324) by monitoring the fifth and seventh harmonics of the RF bias power. The ECR plasma etcher applies 1500 W at 2.45 GHz to excite the plasma plus applies 900 W at 13.56 MHz to the wafer chuck to generate a plasma bias of about 300 V to provide sufficient energy to the ions bombarding the Pt. Figure 1a shows a current and voltage detector in the coaxial power line, and Figure 1b shows such a detector. Figure 5b shows the current of the seventh harmonic of 13.56 MHz (i.e., 94.92 MHz) as a function of time during the Pt etch; the clearing of the Pt results in a large drop in the seventh harmonic of the current. Other current and voltage harmonics also vary during the etching, but the fifth and seventh harmonics appear especially sensitive for this Pt etch.

The use of an RF power harmonic endpoint detector has an advantage over optical endpoint detection in that an optical port in the etch chamber wall will become covered with redeposited Pt and cutoff the optical signal, whereas the power harmonic detector has no such limitation.

The main etch may take up to 2 minutes, and a 1 minute overetch suffices. The etch etches Pt about 10 times faster than it etches TiAlN. The Pt etch has converted Pt layer 326 into bottom electrodes 334; see Figure 3i.

(16) Strip TiAlN 332 and exposed TiAlN 324 with a chlorine based plasma with low plasma bias as described in foregoing step (13); see Figure 3j

(17) Conformally deposit BST dielectric layer 336 by CVD to a thickness of 50 nm; then deposit top electrode Pt layer 338 of a thickness 100 nm by sputtering; see Figure 3k. If a FeRAM with ferroelectric capacitors is desired, then a ferroelectric such as SBT would be deposited rather than BST.

(18) Deposit top barrier TiAlN 340 by sputtering to a thickness of 20 nm, deposit SiON ARC 341 to the appropriate thickness and composition for reflection elimination by PECVD from silane and N₂O (or spin on organic ARC), and then spin on photoresist. Expose and develop photoresist 342 to define a memory cell array; see Figure 3l. Alternatively, if a ferroelectric had been deposited rather than BST, then photoresist could define the locations of the drive lines for a FeRAM cell array.

(19) Use patterned photoresist 342 as a mask to etch exposed ARC 341, underlying TiAlN 340, Pt 338, and BST 336, stopping on dielectric 318 or on partially etched BST 336. Then strip photoresist 342 and underlying ARC 341; see Figure 3m.

(20) Deposit inter metal level dielectric (ILD) 344 and planarize by CMP.

(21) Photolithographically define holes (contacts, vias) and fill with metal 348 such as by a blanket deposition followed by planarization or etch back.

(22) Blanket deposit a first metal level, and pattern it to form first level interconnects 352. See Figure 3n.

(23) Metal interconnects 352 may have top cladding 353, such as TiN cladding for aluminum metal. Further metal levels follow the same via formation and fill, planarized inter metal level dielectric, via fill, metal deposition and patterning to form interconnects 354 (with cladding 355) and 356; see Figure 3o.

Silicon oxide/nitride hardmask

[0010] The TiAlN hardmask 332 could be replaced with a hardmask of silicon dioxide or silicon nitride or silicon oxynitride; although the selectivity of the Pt etch will decrease. In this case an organic ARC layer would be used. A silicon dioxide or silicon nitride hardmask does not need the pre etch oxidation treatment.

[0011] [28152] However, with a high temperature (e.g., 250-350 C) version of the Pt etch of foregoing step (15), the volatility of PtCl_x species increases to improve sidewall slope, but the selectivity of the etch decreases. Thus for a high temperature etch add a thick silicon oxide or silicon nitride or silicon oxynitride hardmask on top of the TiAlN 328 to form a bilayer hardmask. Again, use organic ARC. In particular, after depositing a 20 nm thick TiAlN layer 328 deposit a 500-600 nm thick silicon oxide or silicon nitride or silicon oxynitride layer, spin on 60 nm thick organic ARC, and then spin on photoresist. Note that the top TiAlN provides adhesion between Pt and silicon dioxide/silicon nitride and also provides an etch stop during the strip of the silicon oxide or silicon nitride or silicon oxynitride after the Pt etch.

[0012] Expose and develop the photoresist to define the capacitor locations, etch the organic ARC (oxygen plasma), etch the silicon oxide/nitride/oxynitride layer (fluorine-based plasma), etch the TiAlN (chlorine-based plasma), and strip the photoresist and organic ARC (oxygen plasma).

[0013] Etch the Pt using the previously described Ar/Cl₂ plasma with less than 5% O₂ plus N₂ to increase etch rate because O₂ and N₂ will not significantly slow the erosion of the silicon dioxide/nitride/oxynitride hardmask. Etch for a time that should remove about 80% of the Pt (or until the Pt etch endpoint is first detected by RF current harmonics). Then overetch with extra O₂ added to the gas mixture for increased selectivity to bottom TiAlN 324. For example, increase the O₂ to at least 20% of the gas mixture. Also, add N₂ (e.g., 10%) to help maintain the TiAlN 324 which will be the etch stop.

[0014] After the Pt etch, strip the silicon dioxide/nitride/oxy-nitride hardmask; the bottom TiAlN protects the underlying ILD and the top TiAlN is an etch stop on the Pt. Then strip the top and exposed bottom TiAlN.

Softmask preferred embodiment

[0015] [26598] An alternative Pt etch eliminates the hardmask and uses only a photoresist mask during a Cl₂ RIE etch. In general, photoresist-only mask etching of Pt with Cl₂ leads to redeposition on the photoresist sidewall, forming a "fence" of residues which is difficult to remove. The preferred embodiment uses a two-step etch process. During the first step, performed with a Cl₂ flow of 50 sccm at a pressure of 0.5 mTorr and a MW power of 1500 watts and RF power of 900 watts, etch the Pt (plus any adhesion layer) through to the underlying dielectric (e.g., oxide). Then increase the pressure to about 10 mTorr and continue for a 20% overetch. The higher pressure leads to an enhanced photoresist removal rate, which, in turn, serves to remove the Pt residue fence. This approach increases the Pt sidewall slope compared to the one-step approaches which remove the fence, although not as steep as the hardmask etching previously described. Experimentally, this two-step (low pressure, then high pressure overetch) etch yields slopes about 60 degrees with no fence using standard photoresist processing.

[0016] This two-step preferred embodiment Pt etch could be used for lower density devices because the area enhancement is not as great as with steeper sidewalls, but the two-step process with only photoresist masking simplifies the Pt etch processing. This two-step etch could also be used for ferroelectric capacitor stack etches as described in subsequent preferred embodiments.

Light irradiation etch enhancement

[0017] [28153] The PtCl_x reaction products during the Cl₂ + O₂ + N₂ etch of Pt have low volatility and do not readily desorb from the Pt surface. However, illuminating the Pt surface with radiation of wavelengths centered about 265 nm (UV) at a power density on the order of at least 1.5 watts/cm² apparently will induce photochemical reactions to desorb the reaction products and permit etching at low temperatures (e.g., 50 C). This should achieve the same results as the 250-350 C etching.

[0018] For such radiation assisted etching, change the design of the plasma etcher of Figure 1a to laterally offset the ECR power input and put a transparent window in the chamber top directly over the wafer. Thus a radiation source (e.g., KrF excimer laser) can be mounted on the outside of the chamber and illuminate the wafer during etching.

Platinum oxide electrodes

[0019] [28057] Anneals in hydrogen-containing atmospheres during CMOS processing (such as a final aluminum sinter plus transistor improvement anneal in forming gas at 400 C) can lead to degradation of BST, PZT, SBT, and other such materials. Pt electrodes have insufficient hydrogen diffusion barrier properties, but other materials such as PtOx, Ir, IrO₂, Ru, RuO₂, ... do provide hydrogen diffusion barriers. However, the resistivity of PtOx is at least an order of magnitude greater than that of Pt. Thus a preferred embodiment Pt electrode for use with the foregoing preferred embodiments has a thin layer of PtOx at the interface of the BST, PZT, or SBT and the Pt.

[0020] In particular, after etching the lower Pt electrode 334 and removing hardmask 332 (as illustrated in Figure 3j), oxidize the surface of Pt electrode 334 by exposure to activated oxygen, such as from a plasma in an ECR reactor. Indeed, apply 1000 W of MW power and low power RF bias (to create a plasma bias in the range of 0-100 volts) with a pressure of 10 mTorr and an oxygen flow of 100 sccm for 5 minutes. This grows roughly 4-4.5 nm of PtOx when the wafer temperature is 64 C, but grows only about 3.7 nm of PtOx at 400 C and almost none at 650 C. The PtOx appears to be amorphous and primarily PtO₂ with some PtO and thermally metastable. The oxidation appears to be self-limiting, and the 64 C oxidations yields a rougher surface than the 400 C oxidations.

[0021] Immediately following the Pt surface oxidation, continue with deposition of BST dielectric 336 and top Pt electrode 338 as illustrated in Figure 3k. Note that an analogous thin PtOx layer at the interface of the BST and the top Pt electrode can be formed by first sputtering a very thin (e.g., 2 nm) Pt layer and then completely oxidizing it with an oxygen plasma as just used to oxidize the surface of the bottom Pt electrode. Deposition of such a thin Pt layer requires low temperatures, and the Pt may not completely cover the surface. After the oxidation of the thin Pt layer, sputter deposit more Pt to complete the top Pt electrode.

[0022] Various oxygen-containing plasmas can be used such as O₂, O₃, N₂O, and combinations of these along with optional inert gasses. Similarly various types of reactors could be used to create the active oxygen for the Pt oxidation, including remote plasmas and photochemical assistance.

[0023] The hydrogen barrier properties of PtOx can also protect the BST (or PZT or SBT) with the PtOx buried in the Pt electrode away from the interface with the BST. This imbedding the PtOx in the Pt electrode makes fabrication of the top Pt electrode simpler: deposit half of the top Pt, surface oxidize it as with the bottom electrode, and then deposit

the other half of the top Pt. Of course, other multilayers of Pt and PtOx can be fabricated by in the same manner for use as electrodes. Also, the PtOx can act as an oxygen source during a high temperature crystallization anneal of the BST.

[0024] Figures 4a-4h illustrate a capacitor-under-bitline version of the foregoing capacitor-over-bitline structure. In particular, Figure 4a shows vias formed, and Figure 4b illustrates the vias partially filled with doped polysilicon 404. Again, the partial filling may be by a blanket deposition with etch back. This is analogous to Figure 3d showing polysilicon 320 filling vias.

[0025] Figure 4c shows silicide 406 formed by blanket metal deposition followed by silicidation reaction and unreacted metal strip. Figure 4d illustrates diffusion barrier 408 analogous to diffusion barrier 322 of Figure 3e; the diffusion barrier may be made of TiAlN and formed by blanket deposition and planarization such as by CMP.

[0026] Figure 4e illustrates platinum bottom electrodes 412 with adhesion TiAlN 410 after etching; this is analogous to Figure 3j. Figure 4f shows the BST 414, platinum top electrode 416, and top diffusion barrier 418 after patterning. The BST and top electrode may be common for all capacitors, and opening 419 is just at the location of the eventual bitline contact; opening 419 separates the top electrode from the eventual bitline contact 432.

[0027] Figure 4g shows planarized dielectric 420. Lastly, Figure 4h shows bitline 430 making contact 432 to the common drain of the transistors after contact etch and fill. The portion of bitline contact 432 through dielectric 400 could have been formed and filled (with polysilicon) simultaneously with the capacitor stems in Figures 4a-4d. In this case the bitline contact through dielectric 420 would be a shallower and simpler to etch rather than through both dielectrics 400 and 420 at the same time.

[0028] The foregoing etches of the Pt bottom electrodes may be adapted to etch materials such as Ir, Ru, ..., and their oxides (as described in the following sections) and used for DRAMs and FeRAMs but also may be adapted to etch materials such as FeNi, FeNiCo, NiCr, ... which are used in magnetic storage devices. That is, the N₂ added to the plasma gasses and/or TiAlN or variant hardmasks used should improve sidewall slopes for essentially sputtering or ion milling etches with Ar and/or Cl.

Second preferred embodiments

[0029] Figures 6a-o illustrate in cross sectional elevation views the steps of second preferred embodiment fabrication methods for integrated circuits (e.g., CMOS or BiCMOS) with memory cells (e.g., FeRAM cells) as follows.

- (1) Follow steps (1)-(7) of the foregoing first preferred embodiments to have a structure as illustrated in Figure 3e. Optionally, dielectric 318 includes a 30 nm thick top layer 602 to act as a diffusion barrier. Layer 602 could be TiO₂, Al₂O₃, and so forth.
- (2) Form a stack of layers as follows:

- Sputter deposit 50 nm thick layer 604 of Ti_{0.6}Al_{0.4}N (bottom conducting diffusion barrier);
- Sputter deposit 100 nm thick layer 606 of Ir (bottom electrode, Pt is not as good as Ir for PZT);
- MOCVD 100 nm thick layer 608 of PZT (ferroelectric);
- Sputter deposit 50 nm thick layer 610 of Ir (top electrode), additionally, a 10 nm thick layer 612 of IrO₂ may be included;
- Sputter deposit 50 nm thick layer 614 of Ti_{0.6}Al_{0.4}N (top conducting diffusion barrier); alternatively, the TiAlN could be 200 nm thick and used also as the hardmask;
- CVD 200 nm thick layer 616 of silicon dioxide (hardmask). See Figure 6a which shows TiO₂ diffusion barrier 602.

An alternative to MOCVD PZT is MOD PZT: spin on precursors and polymerize. Then cure and anneal at 600 °C in a N₂ atmosphere. IrO₂ in an electrode acts as an oxygen source to avoid oxygen depletion of PZT 608, and the anneal improves the PZT characteristics by crystallizing the essentially amorphous PZT.

(3) Spin on photoresist, then expose and develop the photoresist to define the FeRAM capacitor locations. The capacitors may have a 100 nm by 250 nm rectangular footprint.

(4) Use the patterned photoresist 620 as a mask to etch oxide hardmask layer 616 to form oxide hardmasks 622; a CF₄ + CHF₃ based plasma oxide etch works, and overetching into TiAlN 614 is not a problem. Figure 6b shows the photoresist masks offset from perfect alignment over the capacitor stems 315, 320. Then strip the photoresist.

(5) Use oxide hardmasks 622 to etch the TiAlN/Ir/PZT-Ir/TiAlN stack in an ECR single wafer plasma etcher with a multistep etch as follows. First, use a Cl₂ plasma etch at 10 mTorr pressure and 50 sccm flow and low RF bias power (300 W) but high MW power (1500 W) to etch the top TiAlN 614 with the decrease of optical emission at the 414 nm line for endpoint detection; include a 10 second overetch. Next, drop the pressure to 0.5 mTorr with flows of 25 sccm Cl₂ plus 25 sccm O₂ and increase the RF bias power to 900 W to etch Ir 610 and add a 15 second

overetch. Detect the endpoint by the decrease of optical emission of Ir at 378 and 351 nm and the increase optical emission of PZT at 367 nm. Then maintain the pressure and power but shift to flows of 10 sccm Cl₂, 20 sccm O₂, 25 sccm CF₄, and 50 sccm Ar to etch PZT 608 together with a 15 second overetch. Detect the endpoint by optical emission decrease at 367 nm and the increase at 378 and 351 nm. Next, repeat the foregoing Ir etch, and then repeat the foregoing TiAlN etch to strip the exposed TiAlN 604 and stop on the diffusion barrier 602 (if barrier 602 is TiO₂ or Al₂O₃, then this etch may have low selectivity). The etch of the bottom TiAlN will also trench into the TiAlN in the recess over the stems, but the etch is short enough due to the thinness of the bottom TiAlN that only a tolerable amount of the recess TiAlN will be removed. See Figure 6c showing the resulting ferroelectric capacitors 624 and 626.

The stack etch can be summarized by the following table detailing the steps and conditions:

Step	Cl ₂ Sccm	O ₂ sccm	N ₂ Sccm	CF ₄ sccm	Ar sccm	Press. (mTorr)	ECR (W)	RF (W)	Time	Comment
1.	50	0	0	0	0	10	15 00	30 0	OES	Etch exposed TiAlN OES 414 nm
2.		92	8	0	0	10	15 00	0	3 min	Ash PR
3.	25	25	0	0	0	0.5	15 00	90 0	OES	Ir TE etch w/O ₂ : 351, 378 nm decrease ; PZT 367 nm increases
4.	10	20	0	25	50	0.5	15 00	90 0	OES	PZT etch w/O ₂ : 367 nm decrease
5.	50	0	0	0	0	0.5	15 00	90 0	OES	TiAlN remove: 414 nm peak (fast); don't etch through Ir BE 351, 378.

The foregoing steps are all carried out at relatively low temperatures (e.g., less than 200 C) with backside wafer cooling (such as by helium flow). The table uses the abbreviations OES for optical emission spectroscopy, PR for photoresist, TE for top electrode, and BE for bottom electrode.

(6) Deposit a 30 nm thick conformal layer of insulating diffusion barrier TiO₂ 630 by sputter deposit Ti and heat in an O₂ atmosphere; alternatively, use PECVD with precursors TiCl₄ and O₂. Then deposit a 20 nm thick conformal layer 632 of silicon nitride by PECVD with SiCl₄ and N₂. TiO₂ 630 is a diffusion barrier for Pb and thus TiAlN 604, 614 plus sidewall TiO₂ 630 encapsulate PZT 608 which limits Pb out-diffusion. See Figure 6c. Similarly, silicon nitride 632 and TiAlN 604, 614 are hydrogen diffusion barriers and limit later in-diffusion of hydrogen which can degrade PZT 608. The use of SiCl₄ and N₂ for silicon nitride deposition rather than the usual SiH₄ plus NH₃ avoids hydrogen generation during the deposition. Similarly, the use of TiCl₄ plus O₂ rather than MOCVD with O₂ plus metalorganics such as TiEt₄, TiMe₄, TDMAT also avoids the introduction of hydrogen.

Alternative Pb diffusion barrier materials for the capacitor sidewalls include Al₂O₃, Ta₂O₅, ZrO₂, and so forth,

plus materials such as AlN, SiC; and these materials can be analogously deposited either as metals and oxidized or by CVD. The diffusion barriers (for Pb and for H) could be a single material or multilayers.

(7) [27947/28299] Anisotropically etch the deposited silicon nitride 632 and TiO₂ insulating diffusion barrier 630 to leave only a sidewall two-layer dielectric 634; see Figure 6e. This is a two-step etch, the first step is plasma CF₄ + CHF₃ to etch silicon nitride, and the second is plasma of Cl₂ to etch TiO₂. This etch will stop on a silicon nitride barrier 602 but will strip the exposed portion of a TiO₂ barrier 602. An alternative TiO₂ etch is an ECR plasma with high RF bias power and a 0.5 mTorr pressure from 10 sccm Cl₂, 25 sccm CF₄, plus 50 sccm Ar.

The thickness of the resulting sidewall two layer dielectric 634 depends upon the thickness of the conformal depositions and the slope angle of the capacitor sidewalls. In particular, the deposition of the diffusion barrier material will yield a thickness of the diffusion barrier on the sidewalls which is not as thick as on the planar surfaces. The conformality of the deposition is the ratio of the thickness on the sidewalls to the thickness on the planar surfaces. The conformality will in general decrease as the aspect ratio (capacitor height to distance between capacitors) of the gap between capacitors increases. The conformality will also improve as the sidewall slope becomes less steep. Notice that the vertical thickness on the sidewall can be substantially larger than the thickness on the planar surfaces; see Figure 7a.

Figure 7b shows the situation after anisotropic etching. In practice a significant overetch is needed, and Figure 7b includes the results of a 150% overetch. The overetch will always recess the sidewall diffusion barrier from the top of the capacitor. In Figure 7b the recess allows the sidewall diffusion barrier to only cover the top electrode and not the top conductive diffusion barrier. Too much overetch will recess the sidewall diffusion barrier such that it no longer covers the ferroelectric. It is possible to increase the thickness of the top electrode and the top conducting diffusion barrier such to make sure that the sidewall diffusion barrier still covers the ferroelectric even with a large overetch. Similarly, a thick hardmask will insure ferroelectric coverage; see Figure 6e.

Another impact of the overetch on the capacitor structure is that both the top of the capacitor and the underlying substrate will be etched for the amount of the overetch time. The etching rate of the exposed materials is therefore important. Figure 7b shows no etching of the top conducting diffusion barrier but the same etching rate of the interlevel dielectric beneath the capacitor as the sidewall diffusion barrier material.

Figures 7c-7d illustrate the interaction between the sidewall slope, amount of overetch, and conformality on the final sidewall diffusion barrier thickness. Figure 7c shows the relatively large fraction of sidewall material (50%) can be achieved even with 150% overetch if the slope is relatively steep (~75 degrees). If 25% remaining sidewall material is acceptable, then even 64 degree slopes are acceptable with 150% overetch; but in such a case a two layer sidewall (e.g., silicon nitride on TiO₂) should have a much thicker outer layer for it to survive as part of the final sidewall material. Figure 7c also shows that increasing the overetch from 150% to 200% does not drastically reduce the amount of sidewall material. These calculations are for 90% conformality, and this number is consistent with sidewall thickness at 90 degree sidewall angle.

Figure 7d shows the impact of conformality. Smaller conformality results in less material as expected but the sidewall slope is not extremely sensitive to this number.

(8) Deposit interlevel dielectric 640 such as silicon dioxide by PECVD and planarize, such as by CMP, to leave roughly 500 nm of oxide over the capacitors, including the hardmask 622.

(9) Photolithographically define and etch holes (contacts, vias) in planarized dielectric 640 through hardmasks 622 down to conducting diffusion barriers TiAlN 614. This is an oxide plasma etch using CF₄ + CHF₃.

(10) Conformally deposit 20 nm thick TiN barrier metal, and then deposit 300 thick Al:Cu. This fills the vias of the preceding step. Alternatively, fill the vias separately from the metal deposition to form drive lines and interconnects.

(11) Pattern the metal to form drive lines for the ferroelectric capacitors and interconnects away from the memory cell array. See Figure 6f

(12) Form planarized IMD/ILD over drive lines and interconnects.

(13) Form further metal interconnect levels by repetition of the via etch, via fill, metal deposition and patterning. Alternatively, dual damascene processing could be used for the drive lines and interconnects.

Insulating diffusion barrier variations

[0030] [28908] The sidewall insulating diffusion barriers of Figures 6e-6f (and Figure 7b) could be simplified and the entire barrier layer of Figure 6d (and Figure 7a) left in place. In this case the via etch analogous to foregoing step (9) (and Figure 6f) would be through both the ILD and the diffusion barrier. In particular, Figure 14 illustrates alternative onestep and two-step etches with photoresist (PR) mask through ILD (SiO₂) and insulating diffusion barrier TiO₂.

[0031] Indeed, perform either an extensive over-etch of the SiO₂, using standard chemistry and a standard RIE reactor (the lower alternative in the righthand portion of Figure 14), or perform a multi-step etch sequence, in which the TiO₂ is etched separately following initial etch of the SiO₂ layer (the upper alternative in the righthand portion of Figure 14). Various chemistries can be used for the TiO₂ etch, depending on the etch rate and selectivity that is needed.

[0032] This sequence of steps can also be reversed for the case of diffusion barrier etchback prior to ILD deposition.

[0033] The chemistries for the SiO_2 etch should contain a mixture of H- and F-containing gas, and an inert gas (e.g., He, Ne, Ar, Kr, Xe) can be used. The preferred chemistry for a particular reactor (AMAT P5000 RIE system) consisted of 15 sccm CF_4 , 30 sccm CF_3H and 100 sccm Ar flows to give a total process pressure of 100 mTorr.

[0034] Of course, other gases (e.g., CH_2F_2 , CH_3F , CH_4 , C_2F_6 , C_3F_8 , XeF_2 , NF_3 , SF_6), can be the sources of the F and/or H species. An etch chemistry which substitutes or adds compounds containing Cl, Br or I species will have similar properties.

[0035] For the TiO_2 , a combination of Cl- and F-containing species is used. Preferred embodiments include a $\text{Cl}_2/\text{CF}_4/\text{Ar}$ mixture of the ratio 10/25/50 sccm or 25/25/5 sccm or a $\text{Cl}_2/\text{O}_2/\text{CF}_4/\text{Ar}$ mixture of the ratio 10/20/25/50 sccm. As mentioned above, other gases can be substituted or added, such as other inert gases, or other sources of Cl, O or F (e.g., XeF_2 , NF_3 , SF_6). An etch chemistry which or adds or substitutes Br-containing species in place of the Cl-containing species will have similar properties. This etch can be also used for PZT of different compositions and doping, as well as other sidewall insulating diffusion barrier (Al_2O_3 , AlN , etc.) or ferroelectric materials (e.g., SBT, BST).

[0036] Figure 15 illustrates the quadratic model for TiO_2 etch selectivity to photoresist. Non-linear dependences on Cl_2 fraction and the halogen fraction, expressed in terms of the Cl_2 and CF_4 flow ($\text{Cl}_2 + \text{CF}_4$), are seen. While the photoresist etch rate is not so sensitive to the change in conditions, the TiO_2 rate is greatest with high (although not 100%) halogen fraction. Predictions of the etch rates and selectivity for various Ar/ Cl_2 / CF_4 mixtures shown in Figure 15 indicate that the most useful area of process space appears to be the lower two-thirds of the triangular mixture plot.

[0037] The total process pressure is an important variable which provides additional control of etch rate and material selectivity. For example, high pressure operation (10 mTorr) increases chemical etching at the expense of physical sputtering, compared with low pressure conditions (0.5 mTorr). Likewise, the plasma power(s) and plasma-substrate bias also control variables which can be used to adjust the process. These variables will depend on the reactor type that is employed. For the ECR-enhanced RIE reactor used for our demonstrations, we used pressures in the range 0.1 to 10 mTorr, microwave power from 300 to 1500 W and RF power from 0 to 900 W. The plasma bias under these conditions ranged from 0 (at 0 W applied RF power) to ~ 325 V (at 900 W RF power).

[0038] The wafer temperature is another variable which will affect etch parameters. These etches described here used a He backside cooling in order to keep a low wafer temperature. Although the maximum temperature was not measured, photoresist on top of the wafer was still easily removed after etching. Increasing the wafer temperature will increase the component of chemical etching at the expense of sputter etching. It should then be possible to reduce the ion energies of the etch gas which will reduce the physical etch component and hence potentially improve the etch selectivities as well.

[0039] Of course, other types of etch reactors can be used to accomplish this etch, with suitable flow ratio and additive optimization, to improve selectivity and etch profile. Some examples are those with a single RF supply (such as inductively-coupled plasma (ICP) or parallel plate reactors) or dual RF supplies, or other enhanced plasma generation sources. While the system employed here uses 13.56 MHz rf and 2.45 GHz microwave generators, other plasma frequencies can be used with similar chemistries to those described here.

[0040] As mentioned above, other gases can be substituted or added, such as other inert gases, or other sources of Cl, or F (see Table below). An etch chemistry which or adds or substitutes Br-containing species in place of the Cl-containing species will have similar properties.

[0041] Remote sensing of etch endpoint can be accomplished in numerous ways, including optical emission spectroscopy (OES), mass spectrometry, or applied RF power sensing. In the case of OES, material-specific signatures have been determined for SiO_2 (483.5 nm) and TiO_2 etching (322, 335, 364, 375, 415 and 430 nm).

[0042] Additional wet-etch or recovery anneal steps may also be used to remove etch damage layers, as appropriate.

[0043] The Ir electrodes (either bottom or top or both) of the foregoing capacitors could be replaced with Ir plus IrO_2 layers in order to have an oxygen source to deter oxygen depletion during crystallization anneals. A preferred embodiment method of making alternating layers of Ir and IrO_2 first deposits Ir (e.g., sputter deposit 50 nm), then oxidize the surface of the Ir with an oxygen plasma to grow about 3 nm of IrO_2 . Another layer of Ir can be deposited by further sputter deposition, and another oxidation can be performed. In this manner any number of alternating Ir and IrO_2 layers can be made. Also, a thin Ir layer can be entirely oxidized, so a stack can begin and end with either Ir or IrO_2 .

[0044] Experiments yielded the following results with an O_2 flow of 100 sccm at a pressure of 10 mTorr and a MW power of 1000 watts and a DC bias of 0 to 100 volts for a 5 minutes plasma oxidation of Ir at substrate temperatures of 64 to 500 C:

Temperature	(C) Bias (V)	Oxide thickness (nm)
64	0	0
64	50	2.8-3.4
64	100	4.4-5.3
250	0	2.4-4.2
250	50	3.1-4.2
500	0	10-15

[0045] Plasma oxidation appears to give smoother IrO₂ surfaces than furnace oxidation and at a much lower temperature.

[0046] Various permutations of the Ir and IrO₂ layers are possible electrodes; in particular, the following: Ir/PZT/IrO₂, IrO₂/PZT/Ir, Ir/PZT/IrO₂/Ir, Ir/PZT/Ir/IrO₂/Ir, Ir/IrO₂/PZT/IrO₂/Ir, Ir/IrO₂/PZT/Ir/IrO₂/Ir, Ir/IrO₂/Ir/PZT/IrO₂/Ir, Ir/IrO₂/Ir/PZT/Ir/IrO₂/Ir.

[0047] More generally, various materials could be used for the top and bottom electrodes such as noble metals (Ir, Pt, Ru, Rh, Pd, Ag, Au) or conducting oxides such as IrO₂, RuO₂, PdO, RhO₂, SrRuO₃, LaSrCoO₃, YBa₂Cu₃O₇, etc. or multiple layers or alloys of these materials.

[0048] For the small geometry features of high density memories, the ferroelectric material needs to be smooth with a uniform grain structure. Small grain size is important in obtaining smooth surfaces. Smooth surfaces are needed in order to have a uniform electric field through the ferroelectric film as well as maintaining a low leakage current through the film. Thickness non-uniformities also degrade reliability because they create regions with large electric fields.

[0049] Standard thermal MOCVD PZT has fairly large grain size (roughly 100 nm diameter) and rough surfaces (peak-to-valley variation of roughly 40 nm). To produce fine-grain films by MOCVD, the preferred embodiments enhance nucleation density with approaches which include: (1) Use plasma pre-treatment of the bottom electrode prior to thermal MOCVD or plasma-enhanced MOCVD ferroelectric deposition. (2) Use an initial growth step of plasma-enhanced MOCVD ferroelectric deposition prior to thermal MOCVD ferroelectric deposition. (3) Use plasma pre-treatment of the bottom electrode prior to sputtered or reactive sputtered ferroelectric deposition.

[0050] A heuristic illustration of how low nucleation density impacts roughness and grain size is shown in Figures 11a-11d. These figures assume that nuclei grow three dimensionally with a roughly isotropic growth rate. SBT when grown in the crystalline phase will form in a very non-isotropic faceted manner. This will result in similar trends but different quantitative relationships between average film thickness, grain size, and surface roughness. Nucleation occurs randomly at the start as per Figure 11a. During growth the nuclei grow until they impinge on each other, at which point grain boundaries are formed as in Figure 11b. As the film becomes thicker the grains finally cover the surface of the film as shown by Figure 11c. This is the low-thickness limit for producing functional devices; prior to this point, metal deposited on top will result in a metal / metal contact which will create a dead short. The peak to valley roughness at coalescence will be the height of the tallest grain. Further growth will in general result in absolute roughness values that are roughly constant although the scaled roughness (peak-to-valley / average thickness) will improve as illustrated by Figure 11d.

[0051] The impact of larger nucleation rates on grain size and surface roughness are shown in Figures 11e-11f. The higher nucleation density results in smaller grain sizes and also significantly smoother films for the same average film thickness. Because the coalescence point occurs at a smaller grain size, the low-thickness limit for functional devices is extended lower, to thinner films, than in the low-nucleation density case.

[0052] The preferred embodiment treatment of the bottom electrode essentially textures the bottom electrode surface to provide more nucleation sites and thus a larger nucleation density. As described previously, an oxygen plasma treatment may even grow metal oxide on the electrode surface. Various process methods to implement plasma pre-treatment of the bottom electrode are as follows.

(a) Ar and/or O₂ plasma generated by RF (e.g., 13.56 MHz) or microwave (e.g., 2.45 GHz) voltage applied to wafer surface in the MOCVD or plasma-enhanced MOCVD or sputter deposition chamber immediately after loading the wafer and immediately prior to starting MOCVD or sputter deposition. Performing the plasma treatment and PZT deposition without atmospheric exposure in between steps will prevent the surface from adsorbing other gases. The Ar and/or O₂ pressure could be 10 mTorr with a plasma bias of 100 volts for treatment of 2-5 minutes.

-(b) Ar and/or O₂ plasma generated by RF (e.g., 13.56 MHz) or microwave (e.g., 2.45 GHz) voltage in a pre-clean chamber clustered to the MOCVD or plasma-enhanced MOCVD or sputter deposition chamber that occurs soon before the PZT deposition. Clustering the plasma treatment and PZT deposition will prevent the surface from adsorbing other gases.

5 -(c) Ar and/or O₂ plasma generated in an etch chamber separated from the deposition chamber. Plasma might be generated remotely or by applying a RF voltage to wafer or both can be used simultaneously. A remote plasma can be generated by RF, ECR, etc.

10 [0053] Process methods to implement plasma enhanced MOCVD of the ferroelectric for the seed layer are as follows.

[0054] Prior to thermal MOCVD the RF plasma is turned on with Ar and/or O₂ gas flowing into the chamber. The RF energy might be either remote and / or applied to the wafer surface. The precursors are then turned on into the deposition chamber. In order to maximize the nucleation rate and final film properties, the MOCVD process parameters for the plasma-enhanced process need to be optimized separately from the thermal MOCVD process. Therefore the pressure, carrier flows, oxidizer flows, liquid flows and perhaps liquid composition can be different from the thermal MOCVD process values.

[0055] For the preferred embodiment method of initial plasma-enhanced MOCVD followed by thermal MOCVD, the plasma bias could be about 100 volts and the duration only seconds to insure at least partial surface coverage and high nucleation density.

20 [0056] For sputtered PZT deposition, the preferred embodiment grain structure control provides an amorphous lead titanate buffer layer prior to the PZT deposition. In particular, Figure 12a shows a bottom electrode on oxide, the bottom electrode could be Ir, Pt, IrO₂, etc.

[0057] Figure 12b shows a thin (5 nm) layer of Ti (or TiO₂) formed on the bottom electrode, such as by CVD, sputtering, or e-beam evaporation.

25 [0058] Figures 12c-12d illustrates sputtering PbO (or Pb) into the Ti (or TiO₂) to form an amorphous PbTiO₃ (a-PTO) layer containing 10-20% excess Pb atoms (over stoichiometric) and having a thickness of about 8 nm.

[0059] Figure 12e shows 250 nm thick layer of amorphous PZT (a-PZT) formed on the a-PTO by cosputtering Pb(Zr_{0.5}Ti_{0.5})O₃ and PbO targets at 200 C. The PZT was crystallized at 500 C (instead of 520 C required without the PTO seed layer) or by rapid thermal annealing at 600 C in an oxygen atmosphere for 20 seconds (Figure 12f).

30 [0060] Figure 12g shows deposition of top electrode (Ir, Pt, IrO₂, etc.) by sputtering or e-beam evaporation.

[0061] Figure 12h illustrates the stack etch to form the ferroelectric capacitor.

[0062] The PZT ferroelectric could be replaced by other perovskite ferroelectrics such as doped PZT, PZT with the lead replaced (at least in part) by Ca, Sr, Ba, Na, Li, K, La, Ce, Bi or combinations, PZT with the Zr and/or Ti replaced (at least in part) by Zr, Ti, Hf, Ta, Nb, Mn, Fe, Co, Ni, Al or combinations, and combinations of the replacements. Layered perovskites such as Bi₄Ti₃O₁₂, SrBi₂(Ta,Nb)O₉, etc. may also be used. Further, paraelectric versions of these materials could be used for the dielectric of the first preferred embodiments.

35 [0063] An alternative to the sidewall diffusion barrier formation by deposition and anisotropic etching (steps (6)-(7) above) proceeds as follows. First conformally deposit metal such as titanium or aluminum to a thickness of 10-20 nm on the capacitor and dielectric; next, anisotropically etch the metal to leave a metal sidewall; and, lastly, oxidizes the metal to form the sidewall insulating diffusion barrier of TiO₂ or Al₂O₃. Oxidize the metal sidewall with a low temperature (50 C) oxygen plasma (10 Torr pressure and 100 V plasma bias); this avoids also oxidizing exposed TiAlN.

40 [0064] This sidewall alternative allows use of an anisotropic metal etch which can be more selective to the other insulators than the anisotropic insulating diffusion barrier etch. The conformal metal deposition may be by TiCl₄ thermal decomposition or sputtering Ti or Al to avoid hydrogen generation. The anisotropic etches may be plasmas of BCl₃ and Cl₂.

45 [0065] The foregoing preferred embodiments may be varied by using a thick (e.g., 200 nm) top TiAlN diffusion barrier also as the hardmask and eliminating the oxide hardmask. In this case the photoresist is stripped after the TiAlN top etch but prior to the Ir etch by switching to a gas flow of 92 sccm O₂ and 8 sccm N₂ at a pressure of 10 mTorr and 1500 W of MW power but 0 plasma bias. The top TiAlN will survive the bottom TiAlN strip due to its thickness. Also, the Ir and PZT etches may have N₂ added to help deter hardmask erosion as with the previously described Pt etch of the first preferred embodiments.

Alternative stacks and plasma etches

55 [0066] The foregoing TiAlN/Ir/PZT/Ir/TiAlN capacitor stack and diffusion barrier materials and plasma etches may be modified in various ways including the following.

(a) Presume a stack of Ir/PZT/Ir of thicknesses 50 nm/150 nm/150 nm on a stem with bottom diffusion barrier

already formed baut with no top diffusion barrier/hardmask; any sidewall diffusion barriers will be formed after capacitor etching, and a top diffusion barrier will come with the top metal contact. Etch the stack using 900 nm thick photoresist and no hardmask as follows: first use a Cl₂ plasma etch at 0.5 mTorr pressure and 50 sccm flow and high RF bias power (900 W) and MW power (1500 W) to etch the top Ir with the decrease of optical emission of Ir at 378 and 351 nm and the increase optical emission of PZT at 367 nm. Next, maintain the pressure and power but shift to flows of 10 sccm Cl₂, 25 sccm CF₄, and 50 sccm Ar to etch the PZT together with a 15 second overetch; detect the endpoint by optical emission decrease at 367 nm and the increase at 378 and 351 nm. Then repeat the foregoing Ir etch. Lastly, ash the photoresist in an asher.

This etch can be summarized in the following table:

Step	Cl ₂ sccm	O ₂ sccm	N ₂ sccm	CF ₄ sccm	Ar sccm	Press. (mTorr)	ECR (W)	RF (W)	Time	Com-ment
1.	50	0	0	0	0	0.5	15 00	90 0	OES	Ir TE etch: 351, 378 nm decrease; PZT 367 nm increases
2.	10	0	0	25	50	0.5	15 00	90 0	OES	PZT etch, no O ₂ ; 367 nm dec.
3.	50	0	0	0	0	0.5	15 00	90 0	OES	Ir BE etch: 351, 378 nm decrease.
4.									45min	Ash PR (in Branson asher).

The foregoing table again uses the abbreviations OES, PR, BE, and TE, and the etches are performed at low temperatures (e.g., below 200 C) with wafer backside cooling.

(b) Presume a stack of TiN/Ir/PZT/Ir of thicknesses 50 nm/100 nm/100 nm/100 nm on an already formed bottom diffusion barrier, any sidewall diffusion barriers will be formed after stack etching, and a top diffusion barrier will come with the top metal contact. Etch the stack by first oxidize the surface of the TiN and then pattern photoresist on the TiN:O. With the photoresist mask use a Cl₂ plasma etch at 10 mTorr pressure and 50 sccm flow and low RF bias power (300 W) but high MW power (1500 W) to etch the top TiN:O with the decrease of optical emission at the 414 nm line for endpoint detection; include a 10 second overetch. Next, ash the photoresist in an oxygen plasma at 10 mTorr. Then drop the pressure to 0.5 mTorr with flows of 25 sccm Cl₂ plus 25 sccm O₂ and increase the RF bias power to 900 W to etch Ir and add a 15 second overetch; detect the endpoint by the decrease of optical emission of Ir at 378 and 351 nm and the increase optical emission of PZT at 367 nm. Then maintain the pressure and power but shift to flows of 10 sccm Cl₂, 20 sccm O₂, 25 sccm CF₄, and 50 sccm Ar to etch PZT together with a 15 second overetch; detect the endpoint by optical emission decrease at 367 nm and the increase at 378 and 351 nm. Next, repeat the foregoing Ir etch, and then repeat the foregoing TiN:O etch to strip the exposed TiN:O.

[0067] This etch system can be summarized in the following table:

Step	Cl ₂ sccm	O ₂ Sccm	N ₂ sccm	CF ₄ sccm	Ar sccm	Press. (mTorr)	ECR (W)	RF (W)	Time	Comment
1.	50	0	0	0	0	10	15 00	30 0	OES	TiN pattern; 414 peak, stop on Ir: 351, 378 nm increase.
2.	0	92	8	0	0	10	15 00	0	3 min	Ash PR
3.	50	0	0	0	0	0.5	15 00	90 0	OES	Ir TE etch: 351, 378 nm decrease; PZT 367 nm increases
4.	10	0	0	25	50	0.5	15 00	90 0	OES	PZT etch: 367 dec.
5.	50	0	0	0	0	0.5	15 00	90 0	OES	Remove TiN, keep Ir TE intact: 414 peak, 351, 378 nm decrease

[0068] The foregoing table again uses the abbreviations OES, PR, BE, and TE, and the etches may be at low temperatures with wafer backside cooling.

[0069] The individual etch chemistries of the foregoing preferred embodiments can be varied as follows.

[0070] For Ir the Cl₂ etch can have O₂ and N₂ added; the O₂ and N₂ deter erosion of hardmasks such as TiAIN, but oxygen will erode softmasks. The N₂ modifies the noble metal and helps increase sidewall slope. Of course, other gasses can be the sources of the Cl, O, and N species, such as OCl₂, N₂O, Other halogens (Br and I) could also be used in place of or in addition to the Cl.

[0071] For PZT the Cl₂+CF₄+Ar etch can have O₂ added and the mixture varied; the O₂ addition helps deter loss of oxygen from the PZT. Of course, other gasses can be the sources of the Cl, F, Ar, and O species, such as OCl₂, ClF₂, Presumably, the Ar breaks the PZT bonds allowing the Cl and F to react to form volatile products with the Pb, Zr, and Ti. The relative volatilities of the fluorides and chlorides vary for Pb, Zr, and Ti; so the composition of the PZT (Zr to Ti ratio) leads to selection of the F to Cl ratio.

[0072] The following table summarizes various convenient gasses categorized according to function and which

may be used as replacements or additions:

Generic Chemistry	Embodiment	Further examples
Noble Gas	Ar	He, Ne, Ar, Kr, Xe
Chlorine Source	Cl ₂	Cl ₂ , BCl ₃ , HCl, CCl ₄ , S C _x Cl _y
Fluorine Source	CF ₄	SF ₆ , NF ₃ , F ₂ , XeF ₂ , HF, C
Chlorine+Fluorine So	ClF	ClF, CCl ₂ F ₂ , C _x F _y Cl _z
Oxygen Source	O ₂	O ₂ , H ₂ O, CO, CO ₂ , NO, N ₂ O
Noble Metal Modifier	N ₂	NO, CN
Alternate Halogens	Br ₂	Br ₂ , HBr, I ₂ , HI, IBr

[0073] For diffusion barriers (conducting top and bottom TiAlN and insulating sidewall TiO₂), the low pressure, high bias Cl₂ plasma etch can be replaced with a low pressure (0.5 mTorr), high bias (ECR reactor with 1500 W MW power and 900 W RF bias power) plasma of Cl₂ (10 sccm), CF₄ (25 sccm), and Ar (50 sccm). Adding oxygen to this barrier etch yields the PZT etch; this provides convenient multistep etches.

[0074] It is best if the etch process for each layer has a reasonable selectivity for the underlying layers. This allows the use of a more liberal overetch of each layer prior to etching subsequent layers. This overetch will help compensate for non-uniformity in etch rates across the wafer. Under the best case conditions, the non-uniformity of the final etch will be only a little worse than the nonuniformity in the etch process of the last material and not be a combined total of all of the etch processes.

[0075] In terms of maximizing the sidewall profile of materials with low volatilities such as noble metals (Ir, IrO₂, Pt, for example), a large overetch is also desirable. This overetch can only be done if the selectivity between the hardmask and etched material is large. In addition, a large selectivity to the underlying materials is necessary for a large overetch.

[0076] The choice of materials for hardmask materials is very dependent on etch chemistries, etch processes and resulting etch selectivities. The choice of electrode materials and ferroelectrics is usually determined by optimum properties. The optimum hardmask material is simple to deposit, can be chemically etched to achieve sharp profile yet under etch conditions that work well for underlying materials etches has a good selectivity (low etch rate). The hardmask must also either be easily removed or must be useful or at least not cause problems for further processing.

[0077] Etch recipes used to demonstrate etch selectivities.

Recipe	Cl ₂ (sccm)	CF ₄ (sccm)	CF ₃ H (sccm)	O ₂ (sccm)	N ₂ (sccm)	Ar (sccm)	Pressure (mTorr)	RFPwr (Watts)	ECRPwr (Watts)
D-Via		15	30			100	100	750	-----
EtchSi O ₂		45			5		0.5	100	1500
Ir-TE	50						0.5	900	1500
PZTnoO ₂	10	25		20		50	0.5	900	1500
HP-PZT	10	25		20		50	10	300	1500
Ir-TE-O ₂	25			25			0.5	900	1500
PZT-O ₂	10	25							

[0078] Examples of etch selectivities.

Machine	Recipe	Etc Rates (Å/min)						
		h						
		PR	SiO ₂	TiAlN:	TiAlN	PZT	TiO ₂	Ir
		O						
AMAT	D-Via	1230	1760				100	
PQ	EtchSi O2	1775	1715					
PQ	Ir-TE	2100	760	1450	2650	1050	640	2800
PQ	PZTnoO 2	4100	1215	560			480	2100
PQ	HP-PZT						600	2600
PQ	Ir-TE- O2			100	100	800		1600

Endpoint detection

[0079] Figure 9a illustrates the optical emission spectroscopy (OES) signals for an Ir/PZT/Ir stack etch with a 20-second off time for the plasma during gas mixture shifts. The Ir etch is Cl₂ and the PZT etch is Cl₂+CF₄+Ar+O₂, and both Ir and PZT related OES signals are monitored. The changes in OES signals determine etch step endpoint, and the preferred embodiments then add a timed overetch followed by a plasma off time for gas mixture switching and then plasma reignition and the next etch step. This allows automatic process control.

[0080] In more detail, Figure 9b shows the OES signals that occur during the Ir etch step under two different chemistries. Light emission occurs during plasma etching as, for instance, etch products are excited by electrons or ions in the plasma. Two Ir emission bands (350-352 nm and 378-380 nm) are available, and can be further enhanced with various background subtraction techniques: Figure 9c illustrates the during and after Ir etch spectra, and Figure 9d the 380 nm intensity minus the 381.4 nm intensity as a function of time about the endpoint. The large change of the background subtracted signal clearly indicates the endpoint. Other material-specific wavelengths can be used, depending upon the materials in the stack, and the etch chemistry (which can affect both the nature of the emitting species and the spectral region in which observation of the target species is not obscured). Some emission wavelengths are very sensitive to particular etching materials (e.g., 380 nm for Ir etching in Cl₂ chemistries), while others are not. Other wavelengths are indirectly related to the etched species (e.g., CO emission at 438.5 nm during oxide etch), but are still useful process monitors.

[0081] Figure 9e illustrates OES traces for five emission lines during a stack etch in which the photoresist used to mask the hardmask etch (TiAlN HM Etch) is stripped (PR Ash). In particular, the TiAlN etch endpoint is on the TiAlN and Ir (top electrode) signals, the photoresist ash is timed, the Ir top electrode endpoint is on the Ir and PZT signals, and the PZT etch endpoint is on the PZT and Ir (bottom electrode) signals.

[0082] Experiments as in the following table were performed using OES endpoint detection except for photoresist ash:

Step	Cl2 sccm	O2 Scm	N2 sccm	CF4 sccm	Ar sccm	Press. (mTorr)	ECR (W)	RF (W)	Time	Comment
1.	50	0	0	0	0	0.5	15 00	90 0	OES	Etch exposed TiAIN OES 414 nm decrease
2.	0	92	8	0	0	10	15 00	0	3 min	Ash PR
3a.	25	25	0	0	0	0.5	15 00	90 0	OES	Ir TE etch with O2: 351, 378 nm decrease ; PZT 367 nm increases
3b	25	25	10	0	0	0.5	15 00	90 0	OES	Ir TE etch w/O2 & N2..
4a	10	20	0	25	50	0.5	15 00	90 0	OES	PZT etch w/ O2
4b	10	0	0	25	50	0.5	15 00	90 0	OES	PZT etch no O2
4c	10	20	10	25	50	0.5	15 00	90 0	OES	PZT etch w/ N2
4d	10	20	0	25	50	0.5	15 00	30 0	OES	Lo bias PZT etch w/ O2
5	50	0	0	0	0	10	15 00	30 0	OES	TiAIN remove; 414 or 363 nm peak

[0083] The foregoing table of etch variations had the OES signals for the Ir top electrode and PZT etches as shown in Figure 9f. Note that the combination step 3a and step 4d resulted in most of the top electrode being lost and also a anomalous signal traces in Figure 9f (bottom traces).

[0084] Alternatively, the RF harmonics could be used for endpoint detection analogous to Figure 5b. Further, reflectometry or spectral reflectometry or mass spectrometry could be used for endpoint detection.

[0085] In general, these endpoint detection methods sense one of:

(1) the gas environment (OES, mass spectrometry), (2) the plasma characteristics (RF power harmonics, electron energy distribution, discharge current), and (3) etched wafer characteristics (reflectometry). The following table summarizes various convenient methods:

General Sensing Method	Preferred Embodiments	Other Specific Techniques
Gas Environment	Optical emission spectroscopy (OES); Mass spectrometry (in situ)	Residual gas analysis (downstream)
Plasma Environment	RF power harmonics; Electron energy distribution	RF current harmonics; Discharge current measurement
Wafer State Measurement	Reflectometry; scatterometry; Ellipsometry	Spectral reflectometry; Spectral ellipsometry; X-ray fluorescence

Softmask stack etch

[0086] For low density ferroelectric capacitors as could be used in smart cards, a softmask (photoresist only mask on Ir/PZT/Ir or Pt/SBT/Pt stacks) preferred embodiment two-step etch may be used. In particular, photoresist-only mask etching of Pt or Ir with Cl₂ plus etching PZT or SBT with Cl₂ plus O₂ leads to redeposition on the photoresist sidewall, forming the fence of residues which is difficult to remove. The preferred embodiment softmask stack etch uses a two-step etch process. During the first step, performed at a pressure of 0.5 mTorr and a MW power of 1500 watts and RF power of 900 watts, etch the top Pt or Ir with Cl₂ at 50 sccm, next etch the PZT or SBT with Cl₂ at 25 sccm plus O₂ at 25 sccm, then etch the bottom Pt or Ir again with Cl₂ at 50 sccm through to the underlying dielectric (e.g., oxide). Then increase the pressure to about 10 mTorr and continue for a 20% overetch. The higher pressure leads to an enhanced photoresist removal rate, which, in turn, serves to remove the residue fence. This approach yields sidewall slopes about 60 degrees with no fence using standard photoresist processing.

[0087] This two-step etch has the advantages of omitting the hardmask layer deposition and etch steps while still providing a sufficiently steep sidewall so that the self-aligned diffusion barrier as previously described in connection with Figures 7a-7d can be formed.

[0088] As with the first preferred embodiments, the second preferred embodiments adapt to a capacitor under bitline structure fabricated in a manner analogous to that illustrated in Figures 4a-4h. In particular, as previously described first form capacitor stems 1020 plus also bitline stems 1021 as illustrated in Figure 10a.

[0089] Next, form capacitors 1024 and 1026 with sidewall insulating diffusion barriers 1034 as shown in Figure 10b. This employs one of the foregoing stack depositions, stack etches, and sidewall insulating diffusion barriers. Figure 10b illustrates the silicon oxynitride hardmask case.

[0090] Deposit interlevel dielectric 1050 and form drive lines with a dual damascene process as follows. First etch vias down to the bitline stems and capacitor top electrodes (through any insulating hardmasks on the top electrodes). Then etch trenches for drive lines which parallel the word lines. Lastly, fill the vias and trenches with metal (diffusion barriers plus copper) and planarize with CMP to form the drive lines 1060 and filled vias 1062 to the bitline stems; see Figure 10c.

[0091] Deposit interlevel dielectric 1070 and form bitlines with a dual damascene process as follows. First etch vias down to the filled vias on the bitline stems. Then etch trenches for bitlines which are perpendicular to the drive lines and the word lines. Lastly, fill the vias and trenches with metal (diffusion barriers plus copper) and planarize with CMP to form the bitlines 1080; see Figure 10d.

[0092] Figure 8 illustrates in cross sectional elevation views the new step of third preferred embodiments methods for fabrication of integrated circuits (e.g., CMOS or BiCMOS) with capacitors or memory cells (e.g., FeRAM cells) as follows.

(1) Follow step (1) of the second preferred embodiments (which is the same as steps (1)-(7) of the first preferred embodiments).

(2) Sputter deposit 30 nm thick layer 802 of Ti_{0.6}Al_{0.4}N (bottom conducting diffusion barrier) and then sputter deposit 50 nm thick layer 804 of Pt (bottom electrode). Annealing the Pt can increase grain size and modify subsequent SBT characteristics.

(3) Load Pt 804 with bismuth by spin coating 5 ml (for a 6 inch wafer) of a 0.04M solution 806 of Bi(OAc)₃ in a mixture of pyridine and acetic acid (ratio of pyridine to acetic acid of 1 to 2.9 by weight) and drying at 300 C for 5 minutes. Then diffuse Bi into the surface region of the Pt by firing at 700 C for 60 minutes; see Figure 8. The firing time

will determine the amount of Bi infused into the Pt. Then wet clean off the residue (e.g., Bi₂O₃) with basic oxide etch or a water mixture of HCl/HNO₃/HF.

(4) Form the SBT layer on the Bi-infused. Pt as follows. Prepare precursors by mixing bismuth acetate in pyridine and separately dissolving strontium acetate and tantalum ethoxide in glacial acetic acid. Then combine the solutions and spin coat the wafer. Dry at 300 C for 5 minutes and then fire at 700 C in flowing oxygen; this crystallizes the layered perovskite phase. Multiple layers of SBT may be formed to attain a final thickness of about 170 nm. The preloading of the Pt electrode with Bi allows use of a precursor solution with the desired stoichiometric ratio for the SBT without having to compensate for the Bi that would otherwise diffuse out into the Pt. In particular, a mole ratio of 0.9 to 2.1 to 2.0 for Sr to Bi to Ta yields good electrical properties such as large switchable polarization, low coercive voltage, and low operating voltage.

(5) Sputter deposit a 40 nm thick layer of Pt (top electrode), then sputter deposit a 50 nm thick layer of Ti_{0.6}Al_{0.4}N (top conducting diffusion barrier). The top TiAlN will also act as a hardmask for the subsequent stack etch.

(6) Anneal at 550-700 C in a N₂ atmosphere; the anneal improves the SBT characteristics provided that significant Bi is not lost.

(7) Continue as in steps (4)-(14) of the second preferred embodiments. The low pressure Cl₂ + O₂ + N₂ plasma also etches SBT.

[0093] Step (3) of the foregoing provided for bismuth infusion into the Pt bottom electrode prior to deposition of SBT. An alternative to the spin coating method would be to transport Bi by gas phase; that is, use MOCVD to deposit Bi on Pt bottom electrode and diffuse the Bi into the Pt by an anneal. Afterwards, any residual Bi compounds can be stripped in an acid solution. Also, annealing in an atmosphere saturated with Bi could be direct gas phase doping of the Pt. Bi has a vapor pressure of about 20 mTorr at 700 C.

[0094] Alternatives include co-sputter Pt and Bi to form the bottom electrode, and then just use the SBT formation as in step (5). The bottom electrode could have a composition on the order of 1% Bi. Further, the co-sputtering may be replaced by a simpler sequential sputtering process: sputter 10-20 nm Pt, then 1 nm Bi (full coverage is not necessary, this is just an average thickness), then 10-20 nm Pt. In this case the Bi diffuses in the Pt during SBT recrystallization.

[0095] An alternative embodiment provides a Bi atmosphere for the recrystallization anneal of the SBT; this helps maintain the stoichiometry of the SBT against Bi evaporation. Alternative preferred embodiments add to or replace the Bi atmosphere as follows:

(a) Form a graded composition SBT with the bismuth content greater than stoichiometric near the top surface to compensate for subsequent evaporation during recrystallization. For example, with a 150 nm thick SBT layer of composition ratios of Sr=0.9, Bi=2.1, Ta=2.0 the top 5-10 nm could have Bi increased to 2.3 for sufficient excess Bi to compensate for the expected evaporation during a 700 C anneal. More accurately, the initial SBT layer could have the Bi depending on distance from the surface, so that diffusion plus evaporation during recrystallization will yield an essentially uniform Bi content.

(b) After deposition and curing of the SBT layer but before recrystallization, deposit a 10-20 nm thick layer of Bi₂O₃. Then recrystallize at 700 C, the Bi₂O₃ (m.p. about 825 C) provides a Bi source directly on the SBT surface and prevents Bi evaporation. After the recrystallization, strip the Bi₂O₃.

(c) After deposition and curing of the SBT layer but before recrystallization, deposit a 20 nm thick layer of silicon nitride by PECVD. Then recrystallize at 700 C, the silicon nitride provides a Bi diffusion barrier directly on the SBT surface and prevents Bi evaporation. After the recrystallization, strip the silicon nitride with phosphoric acid.

(d) Perform the SBT curing (200 C) but defer the recrystallization anneal until after the top electrode and conducting diffusion barrier (e.g., Bi-doped Pt and TiAlN) have been deposited. The Bi-doped Pt plus TiAlN act form a Bi diffusion barrier to deter Bi evaporation during the recrystallization anneal.

[0096] : Figures 13a-13h illustrate a fourth preferred embodiment PZT or SBT capacitor extending in three dimensions in the shape of a cup instead of the planar capacitors of Figures 6a-6f, 10a-10d. The fourth preferred embodiment may be fabricated as follows.

(1) Start with planar tungsten (W) plug 1302 in a via in interlevel dielectric (ILD) 1304 which may be silicon dioxide. Plug 1302 is formed using CVD W followed by a CMP step. ILD 1304 is typically 1 μm thick and plug 1302 is typically less than 0.2 μm in diameter. Thin silicon nitride layer 1306 is deposited as an etch stop; see Figure 13a.

(2) Second ILD layer 1308 is deposited. The thickness of ILD 1308 is dependent upon the depth required of the cup structure for the desired resulting capacitance (switched charge). For example, for feature size F=0.1 μm, the depth determined by the minimum charge condition (32 fC) is 0.2 μm if the cup is a circular cylinder of diameter 1.9F. The desired switched charge may be 32 fC which may be achieved with a capacitor area of 0.08 μm² by a switched polarization density of 40 uC/cm². Following ILD 1308 deposition (which could be SiO₂ or some low-k material), a

deep ultraviolet lithography approach is used to define an opening in a spun-on photoresist layer. An SiO₂ etch is employed to etch the SiO₂ dielectric while stopping on silicon nitride layer 1306. A second etch chemistry is then used to etch thin SiN layer 1306. The wafer is then cleaned. A conducting diffusion barrier 1310 (CDB), typically TiAlN, TiSiN, TaN, or similar material, is deposited using a CVD approach. The thickness of this CDB layer is typically 10-20 nm; see Figure 13b.

(3) Following CDB 1310 deposition, the cup structure is now ready for CVD electrode deposition. In most cases, a noble metal electrode (Pt, Ir, etc.) is used although a more complex metal-oxide (RuO₂, SrRuO₃) could also be used. The electrode layer 1312 is deposited to a thickness of approximately 20 nm; see Figure 13c. For an SBT ferroelectric, Bi loading could now be performed.

(4) A metal CMP process is employed to remove the portion of electrode layer 1312 outside of the cup region while stopping on conducting diffusion barrier layer 1310; see Figure 13d.

(5) The ferroelectric material 1314, typically PZT, is then deposited using a CVD approach. This deposition is done at a temperature of approximately 550 C in an oxygen ambient, although the variations previously described could be used. The ferroelectric thickness is typically 20-60nm; see Figure 13e.

(6) The top electrode material layer 1316, which is typically similar in composition to the bottom electrode, is deposited using CVD. The top electrode may be deposited so that it is oxygen rich, which could improve device performance and reliability; see Figure 13f.

(7) A deep ultraviolet lithography approach is then employed to etch the ferroelectric stack materials. A photoresist stack etch mask is shown in Figure 13g, although hardmasks such as TiAlN could be used. This etch requires a high-power RIE with varying chemistry as previously described; see Figure 13g.

(8) Following stack etch, an insulating diffusion barrier (Al₂O₃, AlN, etc., typically 10 nm thick) is deposited using CVD. The horizontal portions of the insulating diffusion barrier are removed using a RIE etch leaving insulating diffusion barrier sidewalls 1320 along the top edge of the capacitor; see Figure 13h.

(9) ILD 1322, 300 nm thick, is then deposited using some type of gapfill approach (HDP SiO₂).

(10) A third mask is then used to define a contact via to top electrode 1316. A deep ultraviolet lithography process is used to define the via which is etched using an RIE approach. The etch stops on top electrode 1316. A liner is then deposited and W plug 1324 is also deposited. A W CMP step removes the horizontal metal and planarizes the structure in preparation for multi-level metallization; see Figure 13i.

[0097] The preferred embodiments can be modified in various ways while retaining the features of a multistep via etch through dielectric plus insulating diffusion barrier.

Claims

1. A method of etching a material using a hardmask and a plasma-activated etchant, which method comprising:

provides a hardmask formed of nitrides of titanium and/or aluminum; and etchings said material with an etchant comprising chlorine, oxygen, and nitrogen, is at a temperature on the order of 250-400C.

2. The method of claim 1, wherein said step of providing the hardmask comprises providing a hardmask having an oxidized surface prior to performing said etching step.

3. A method of forming of a capacitor having a bottom diffusion barrier, a bottom electrode, a ferroelectric, a top electrode, and a top diffusion barrier, which method comprising:

etching a stack of diffusion barrier, electrode, ferroelectric, top electrode, diffusion barrier materials with a plasma-activated etchant;
and using optical emission spectroscopy at two or more wavelengths to detect material boundaries and switch etchant composition.

4. A method of forming a capacitor having a bottom diffusion barrier, a bottom electrode, a ferroelectric, a top electrode, and a top diffusion barrier and a sidewall diffusion barrier, which method comprising:

depositing a conformal layer of diffusion barrier material over a capacitor stack of diffusion barrier, bottom electrode, ferroelectric, top electrode, diffusion barrier materials, and
anisotropically removing portions of said diffusion barrier material away from the sidewall of said capacitor stack.

5. The method of claim 4, wherein the step of depositing the conformal layer of diffusion barrier material comprises depositing a sublayer of silicon nitride over a sublayer of metal oxide.
6. A method of forming a capacitor having a bottom electrode, which method comprising:

5

depositing a dielectric;
depositing a top electrode;
surface oxidizing the bottom electrode after formation and prior to dielectric deposition.

10

15

20

25

30

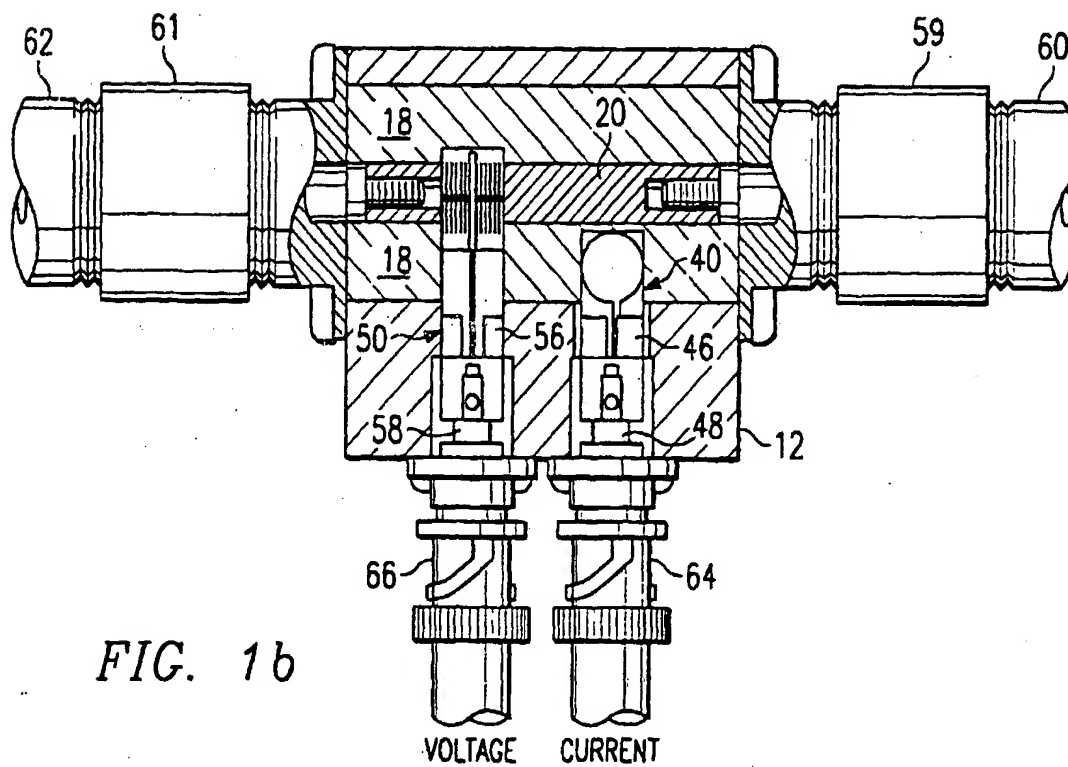
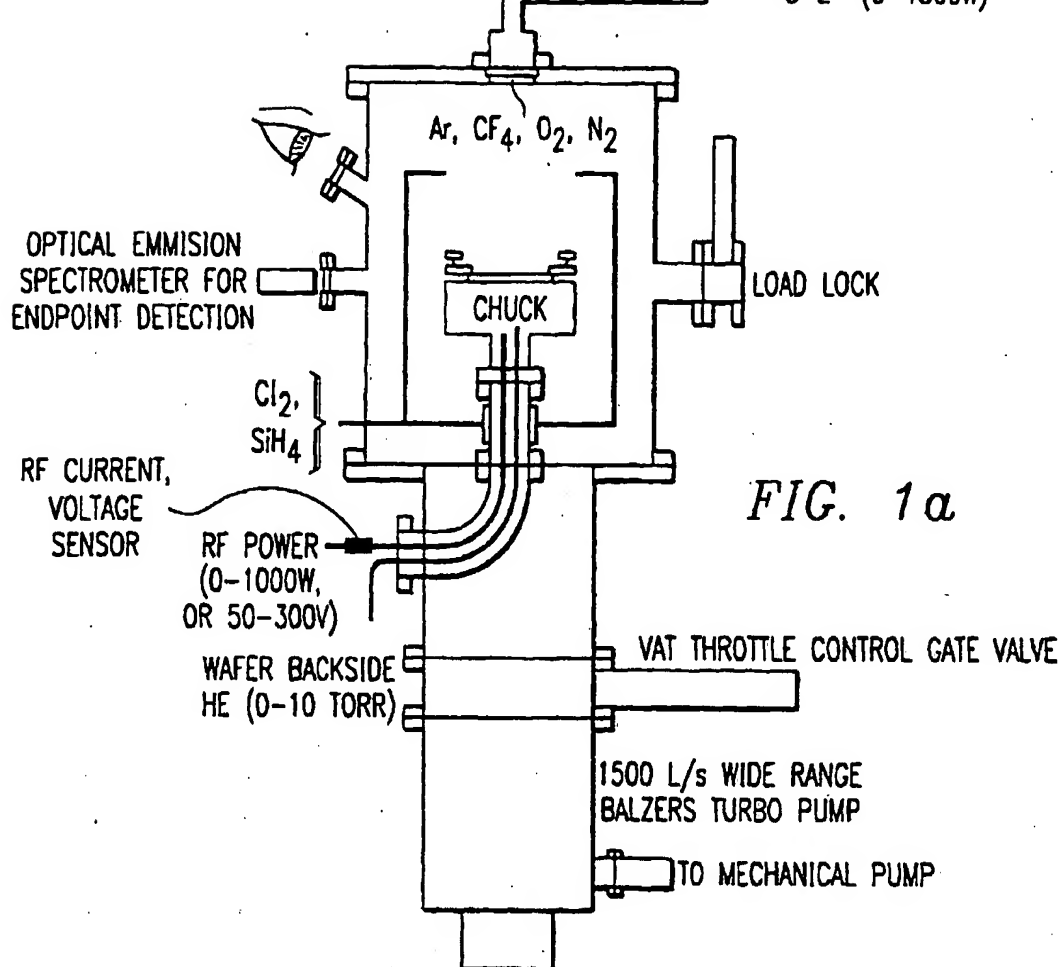
35

40

45

50

55



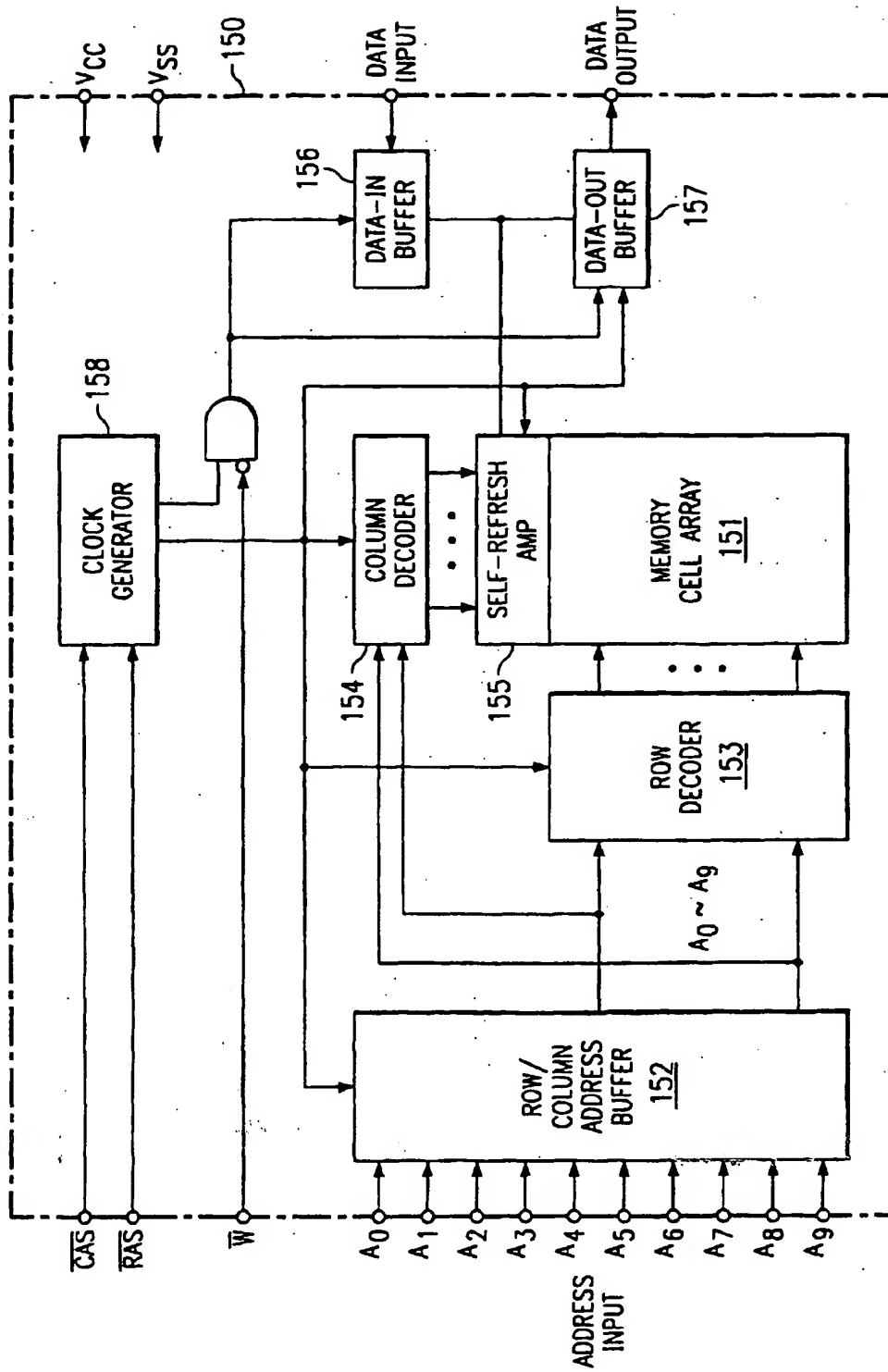
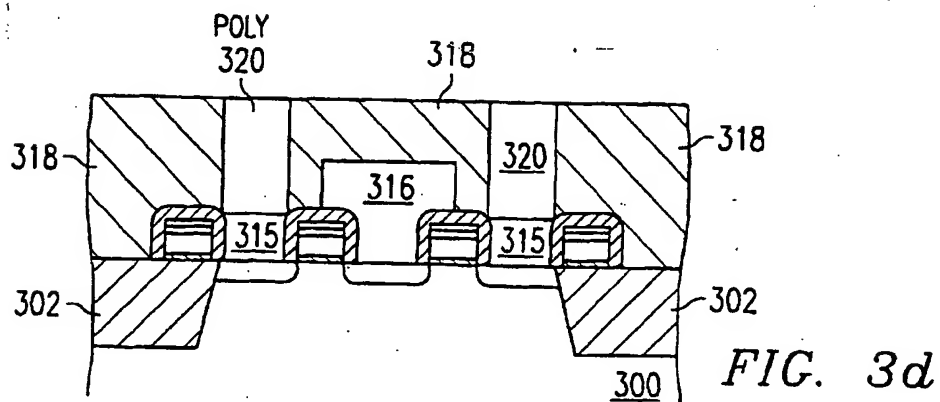
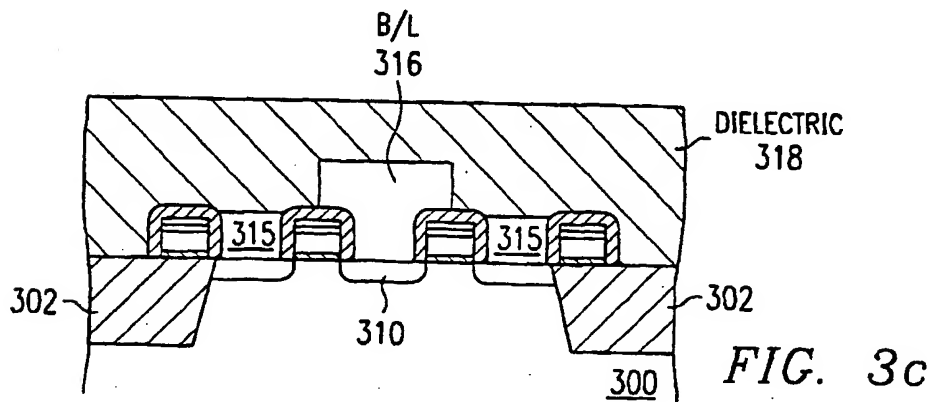
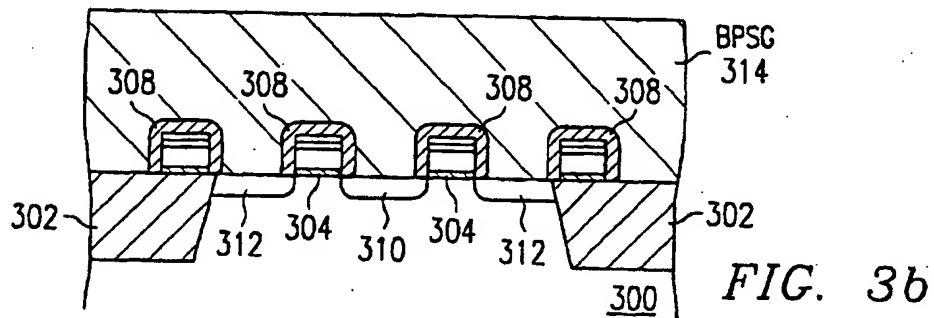
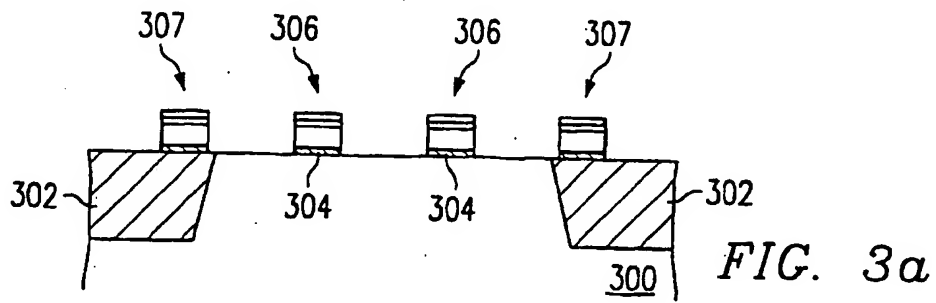
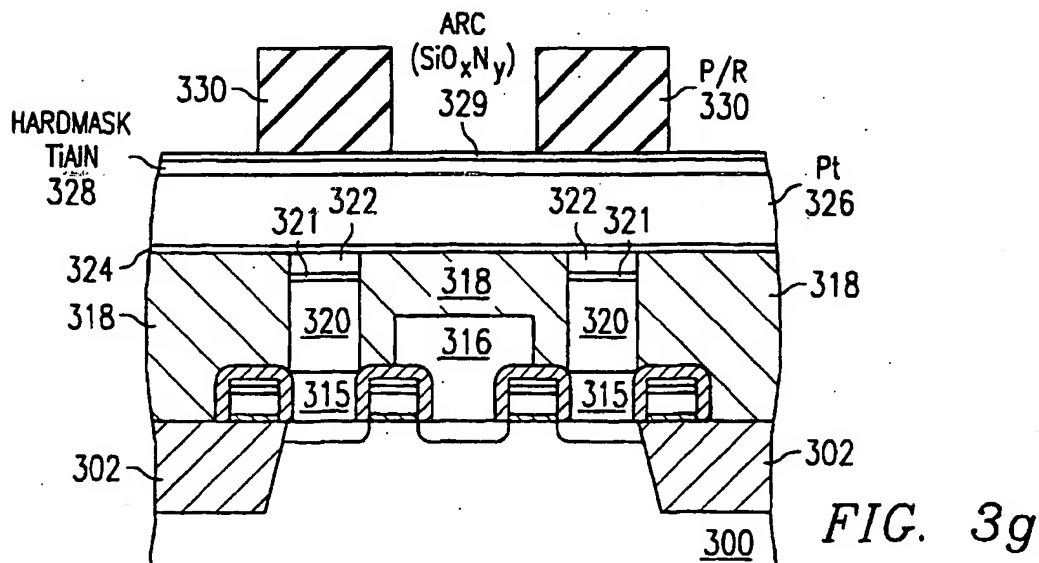
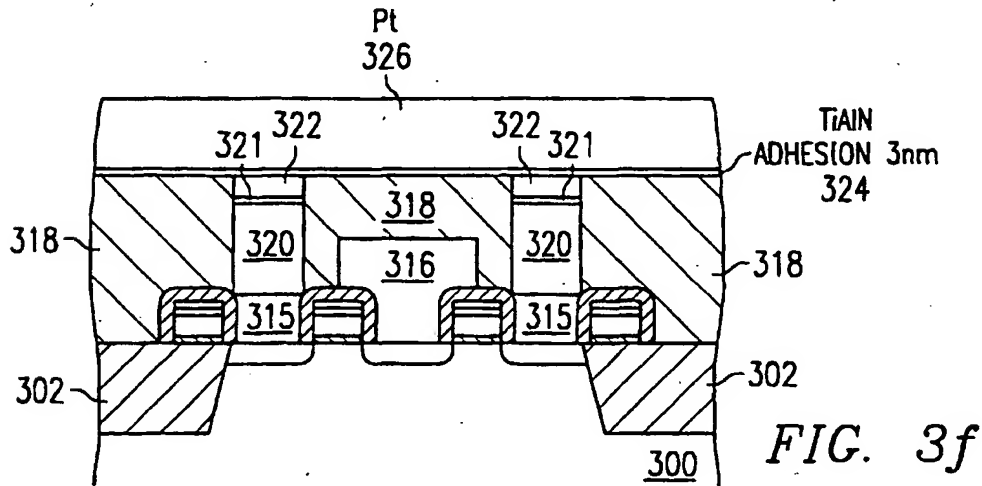
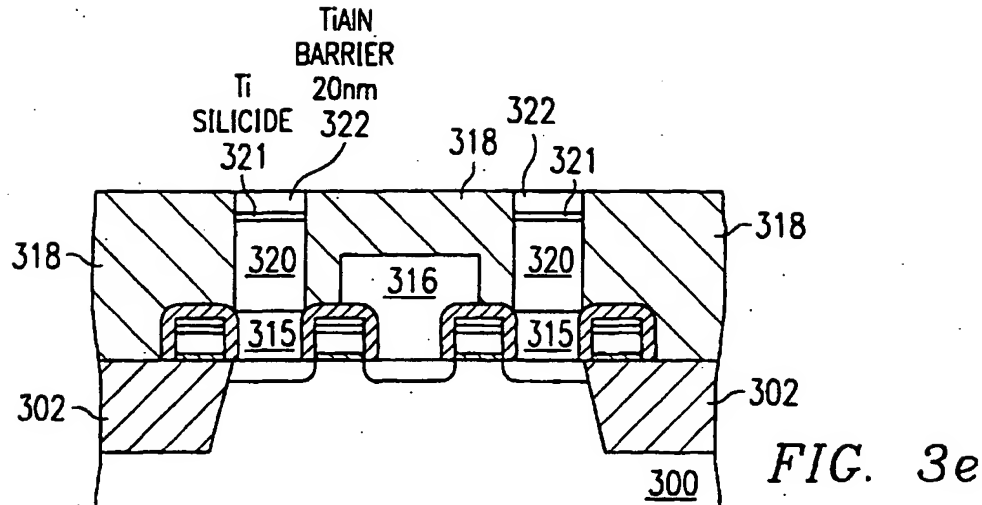
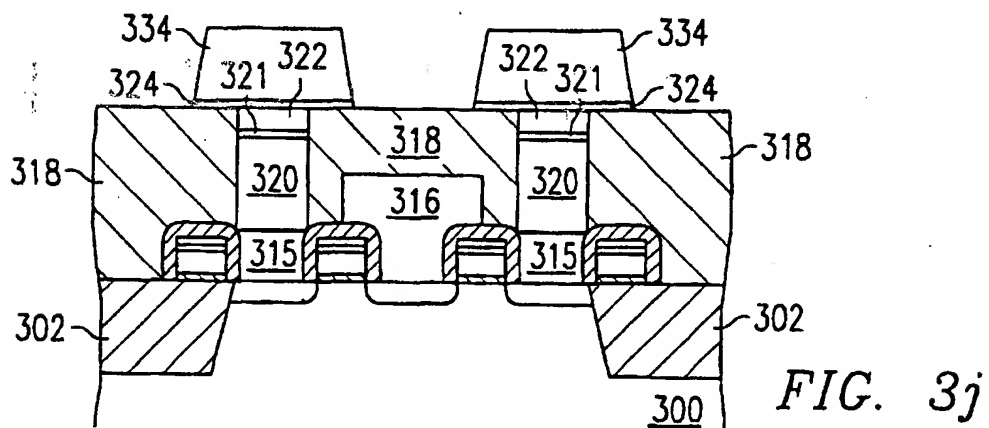
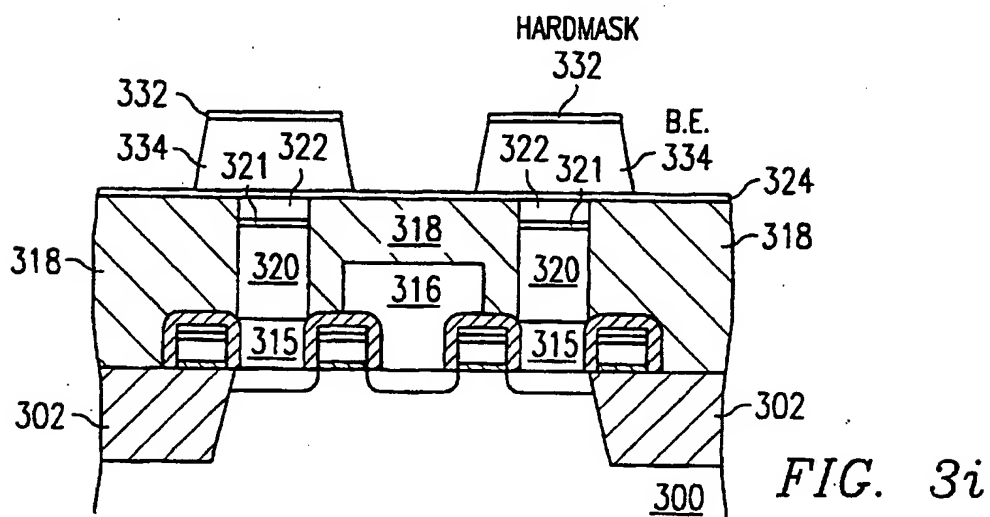
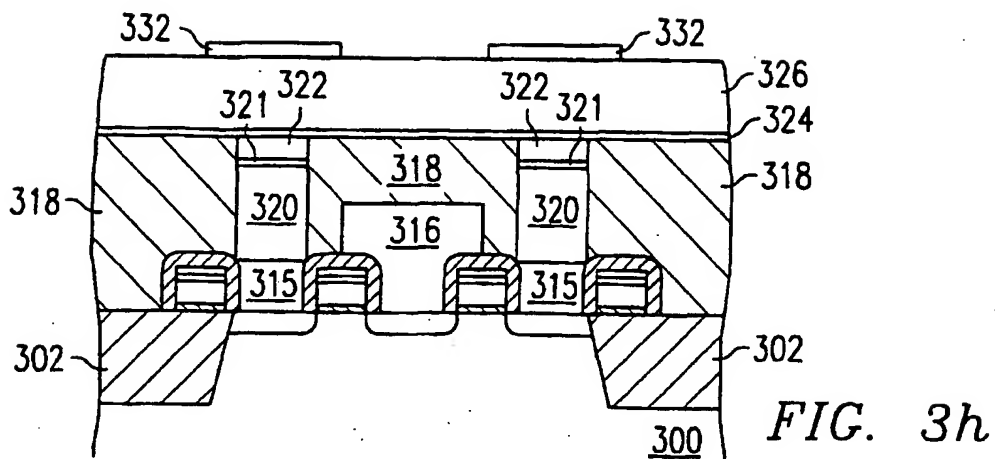
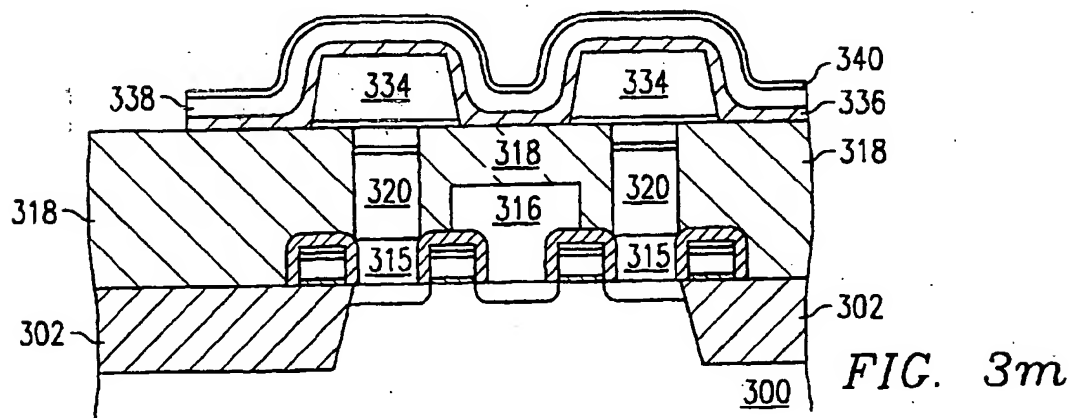
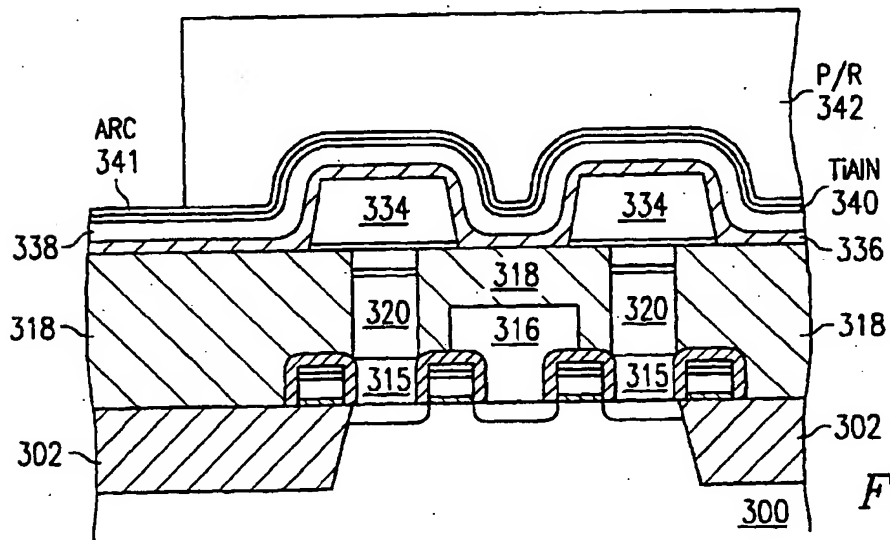
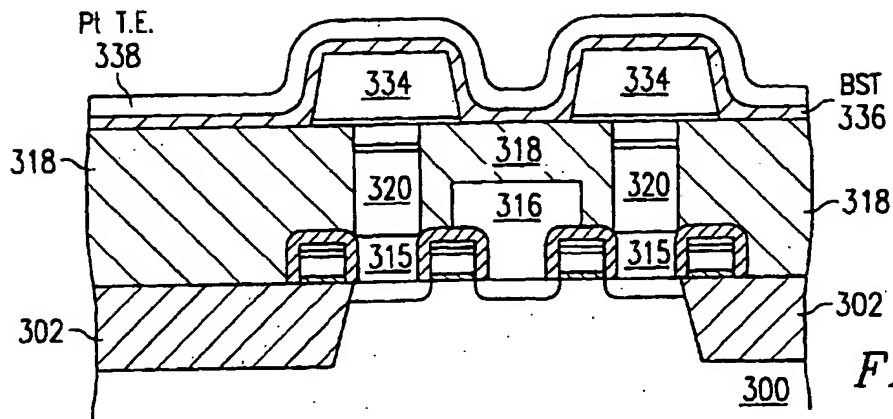


FIG. 2
(PRIOR ART)









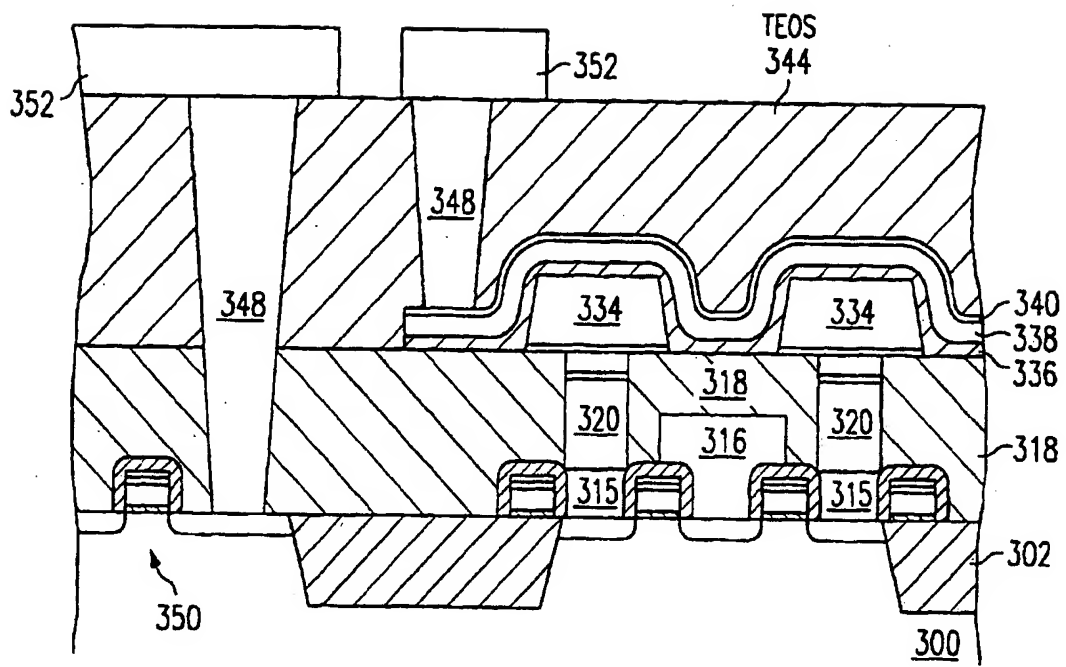


Fig. 3n

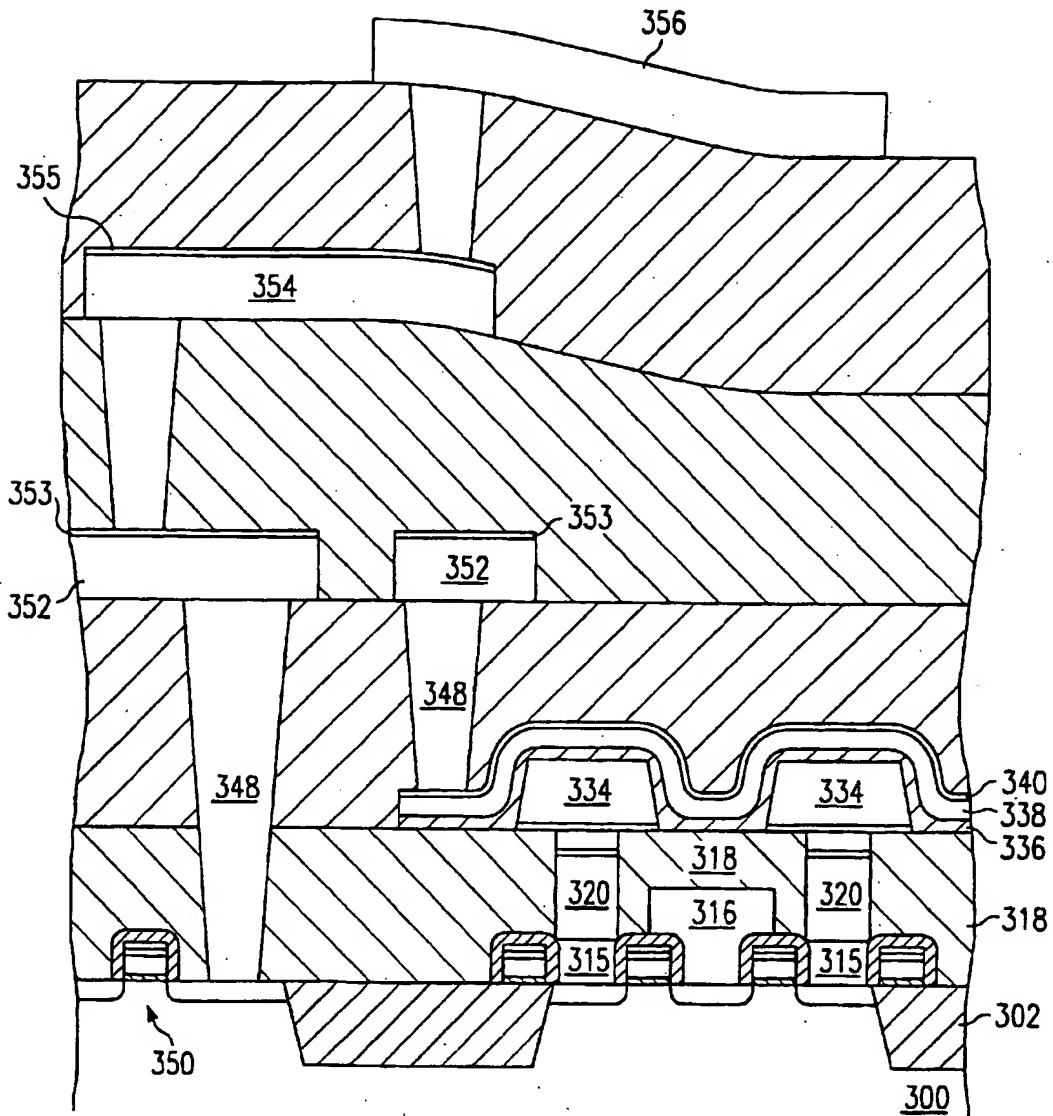


Fig. 30

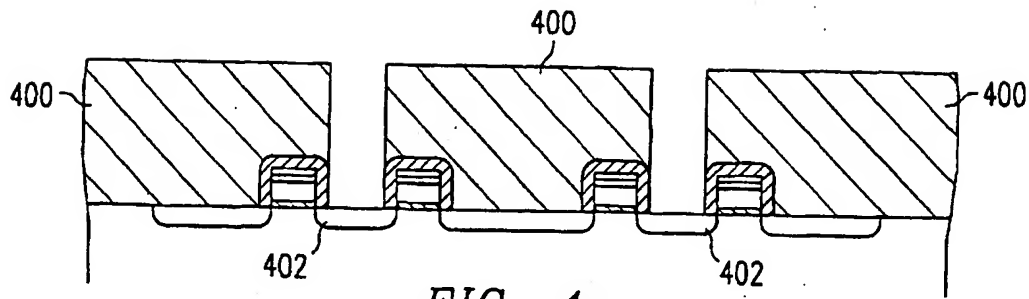


FIG. 4a

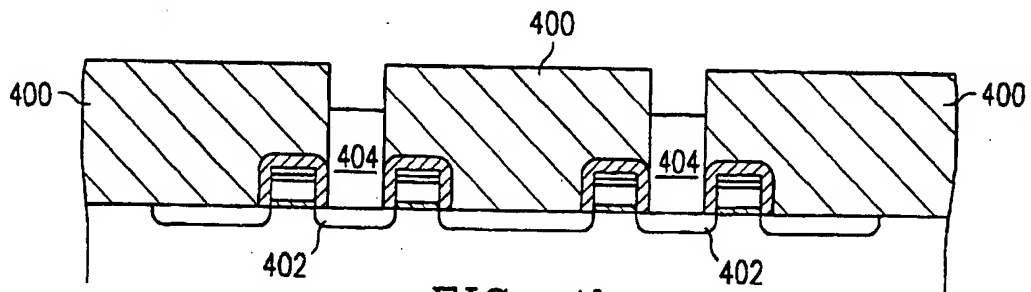


FIG. 4b

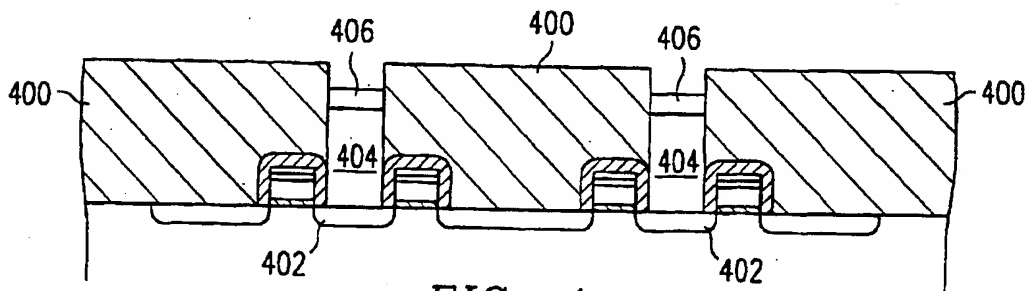


FIG. 4c

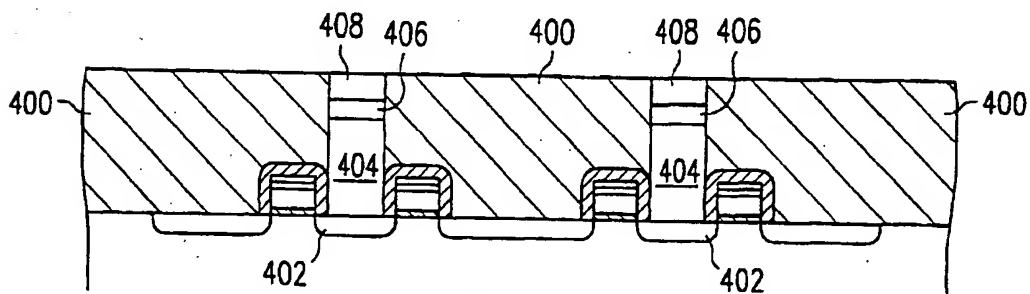
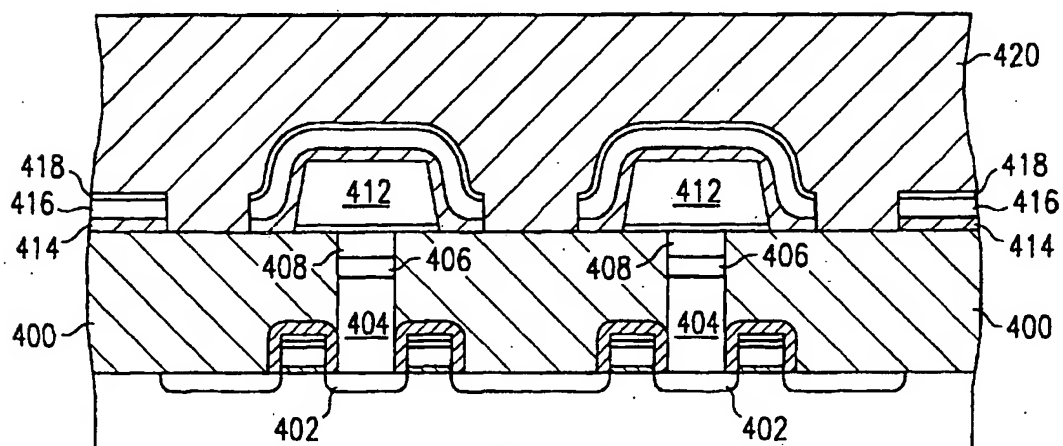
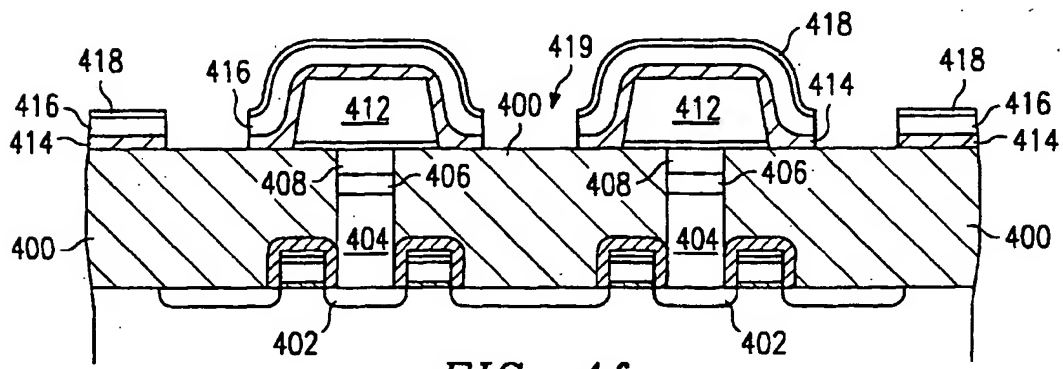
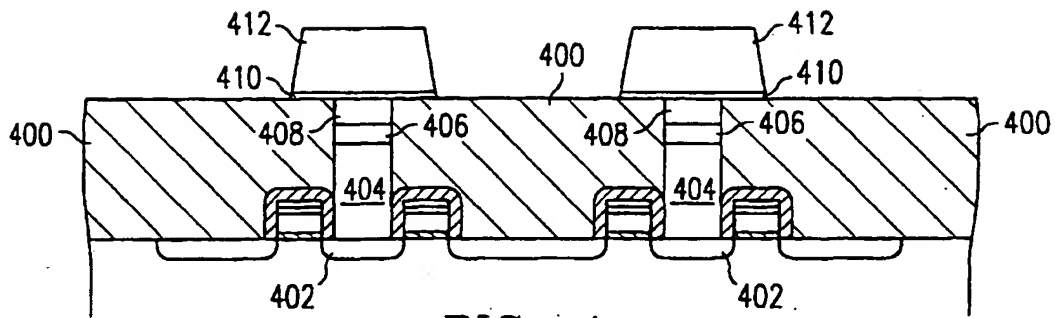


FIG. 4d



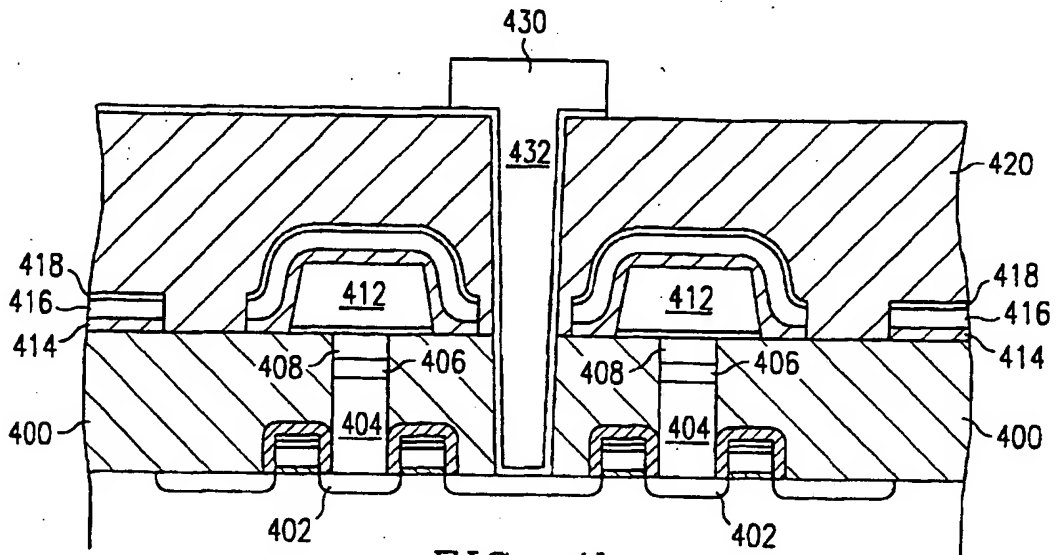


FIG. 4h

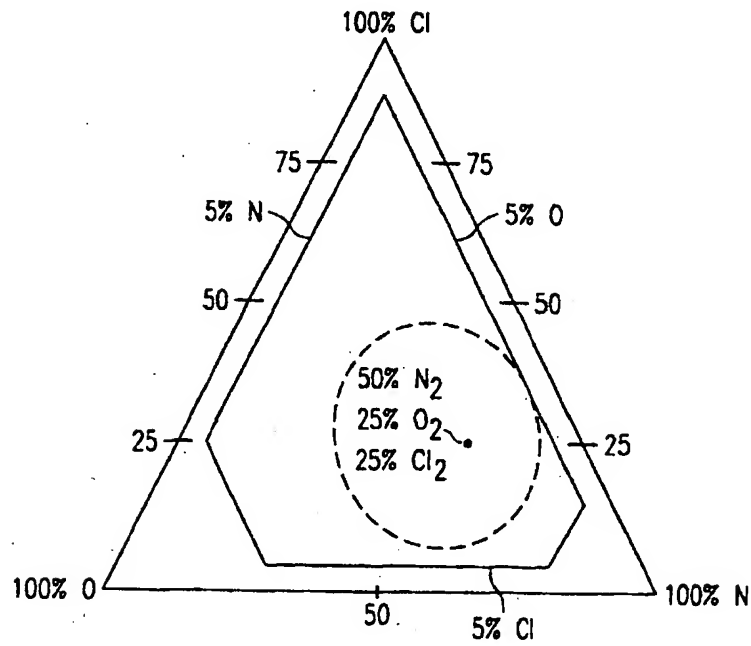


FIG. 5a

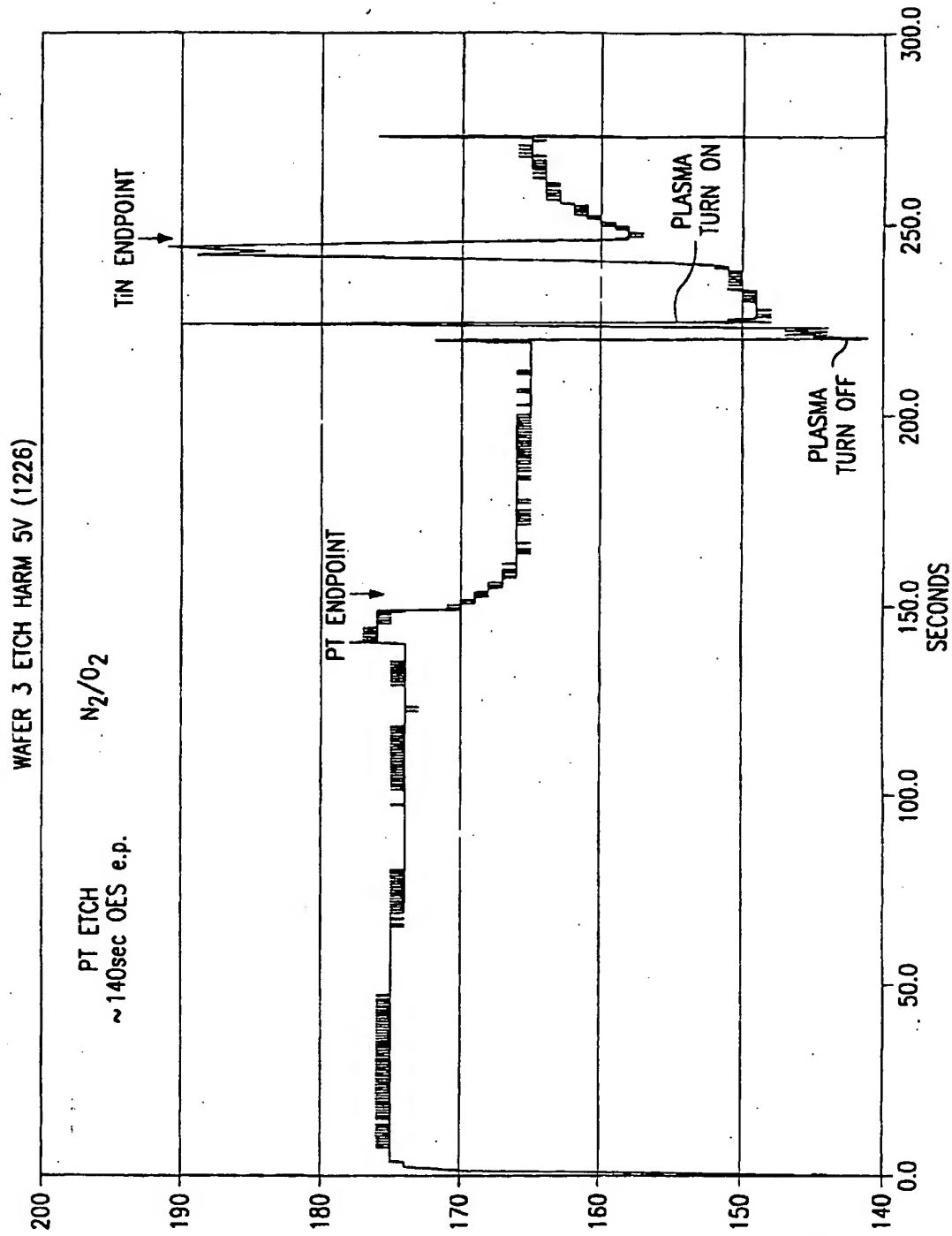


FIG. 5b

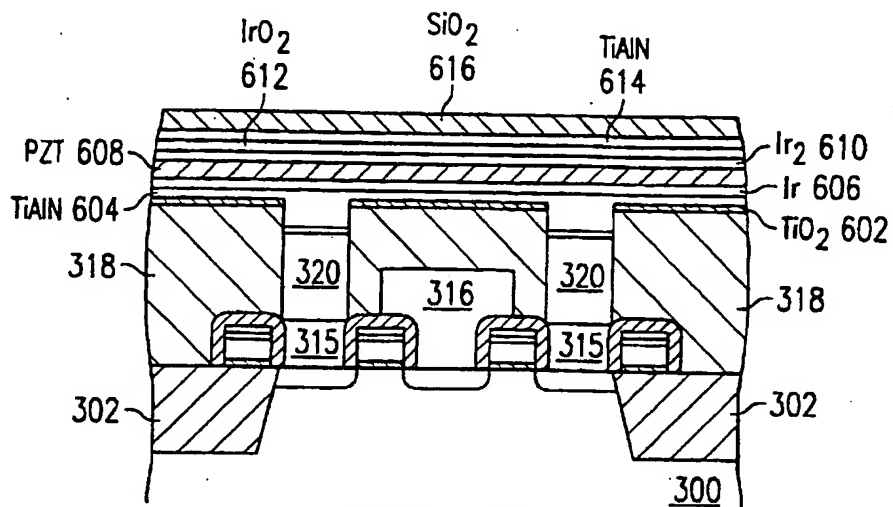


FIG. 6a

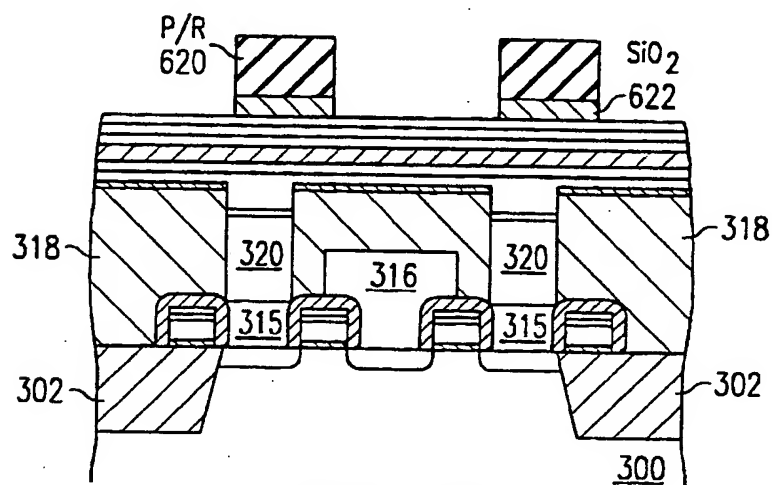


FIG. 6b

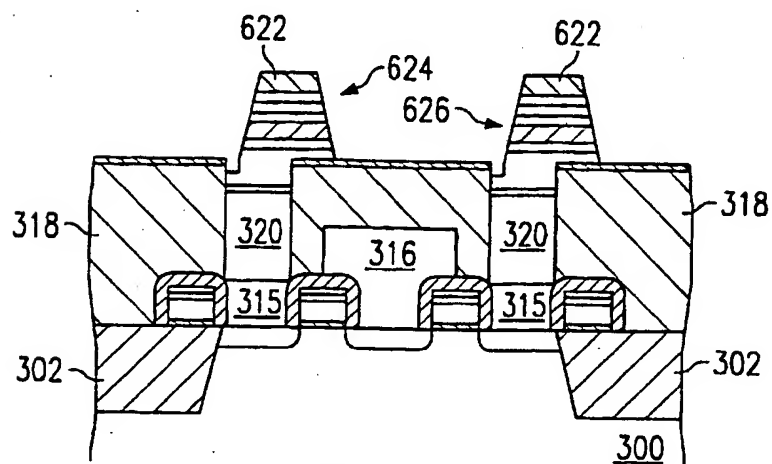


FIG. 6c

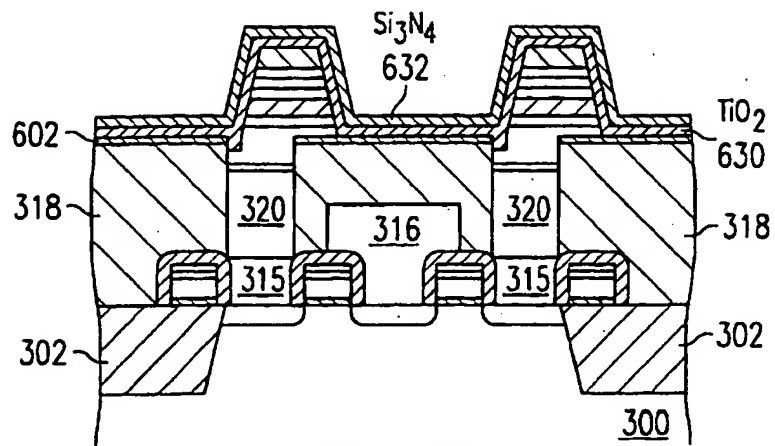


FIG. 6d

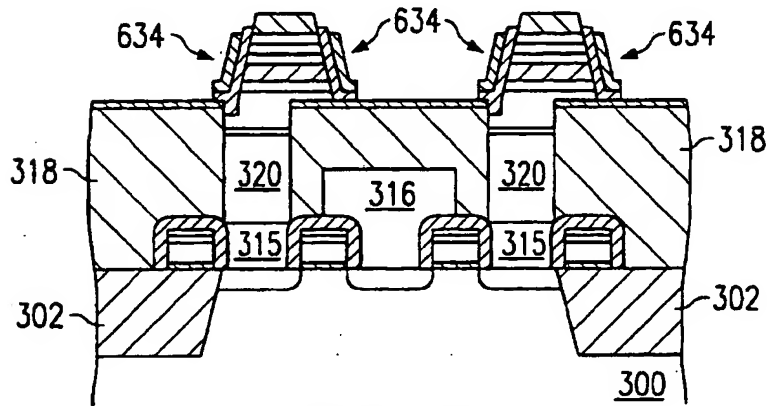


FIG. 6e

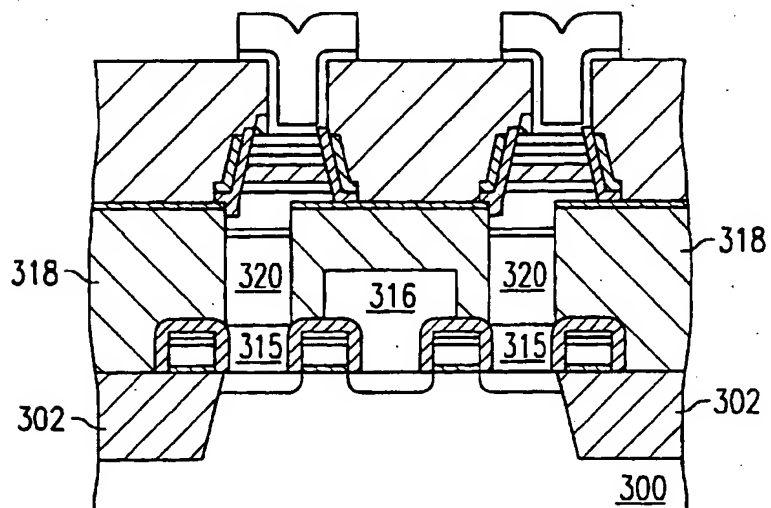


FIG. 6f

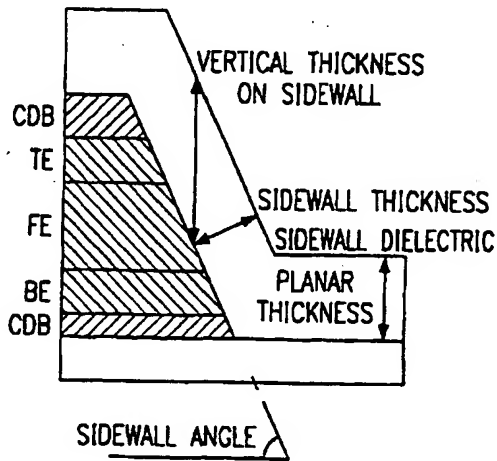


FIG. 7a

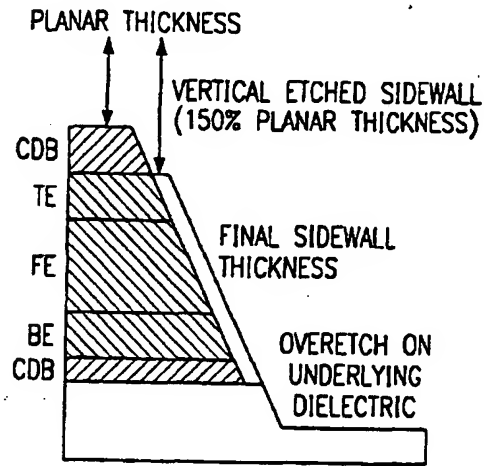


FIG. 7b

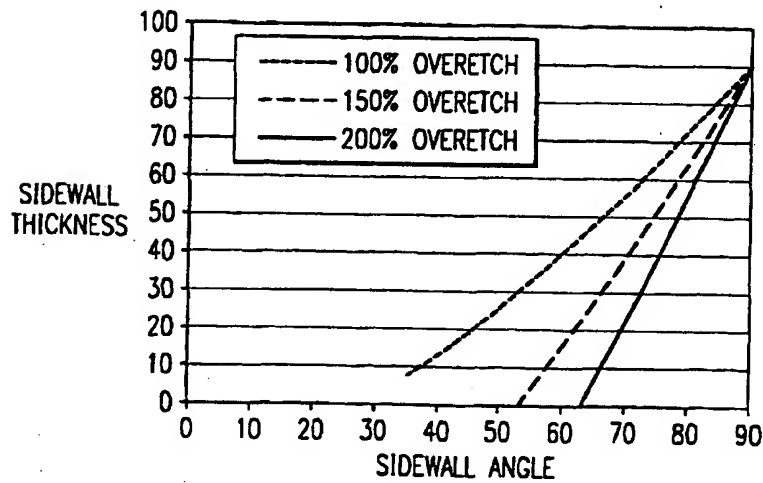


FIG. 7c

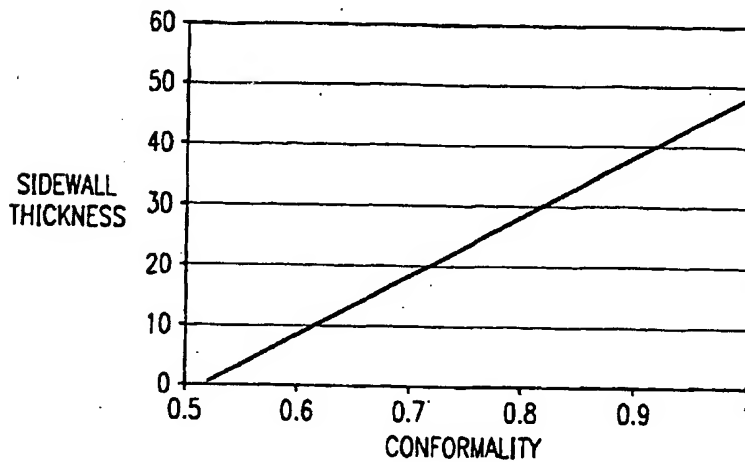
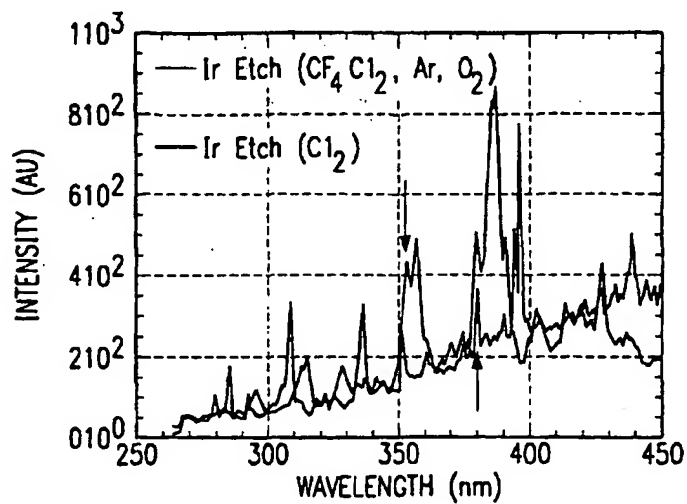
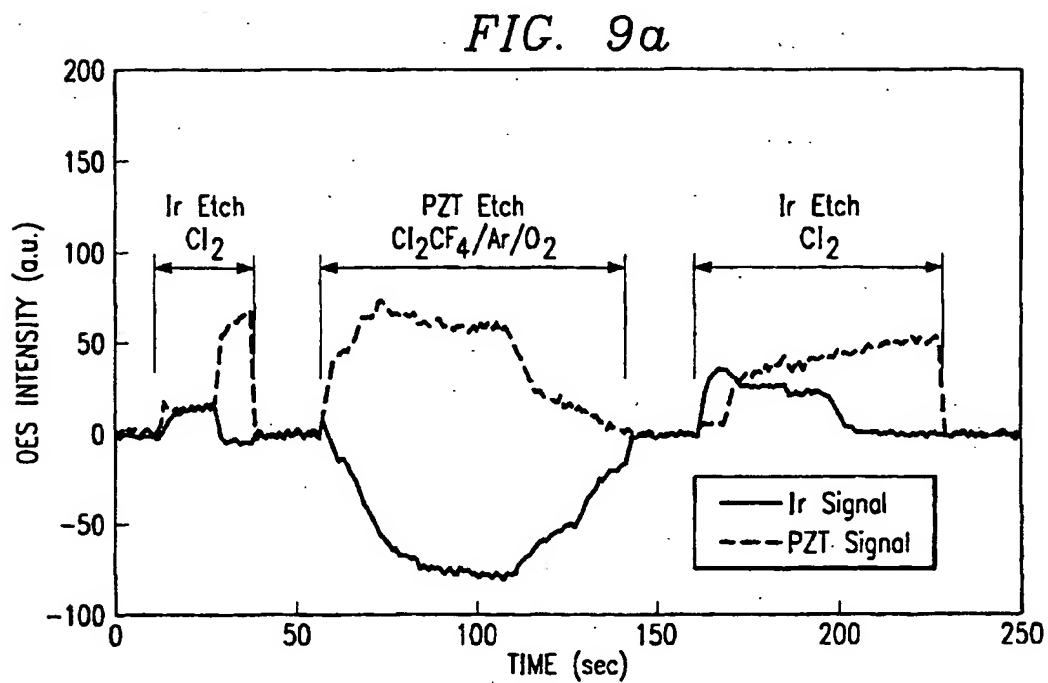
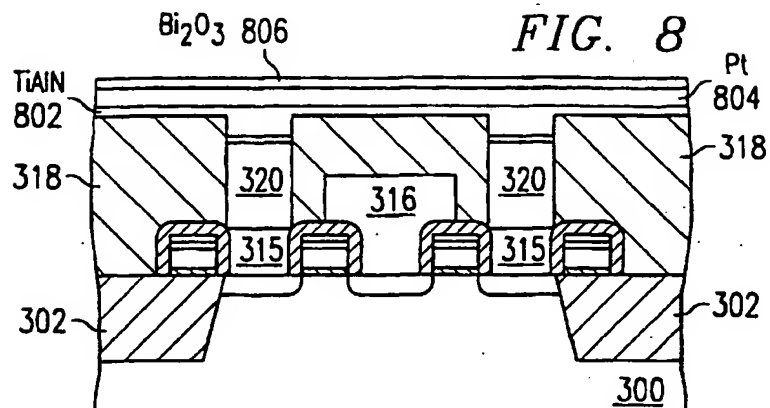


FIG. 7d



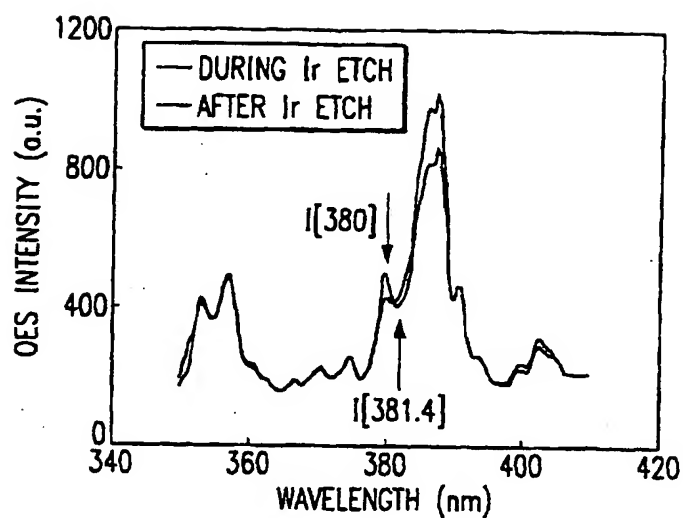


FIG. 9c

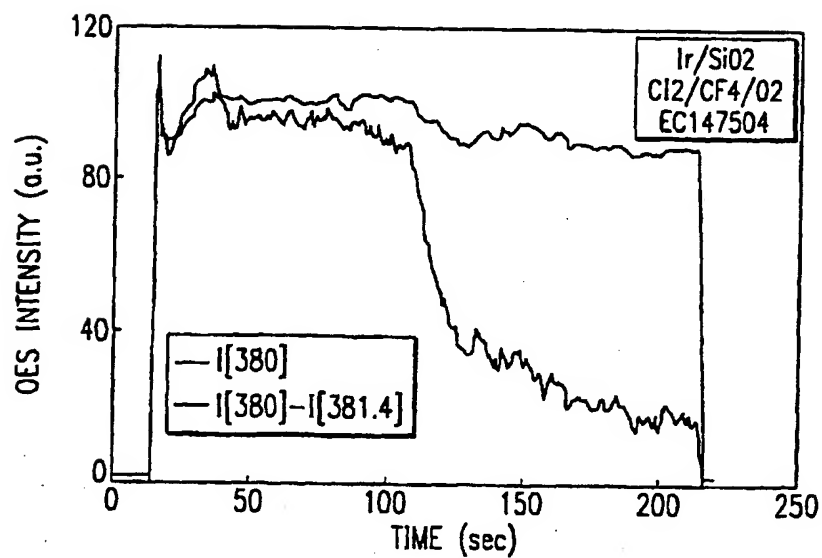


FIG. 9d

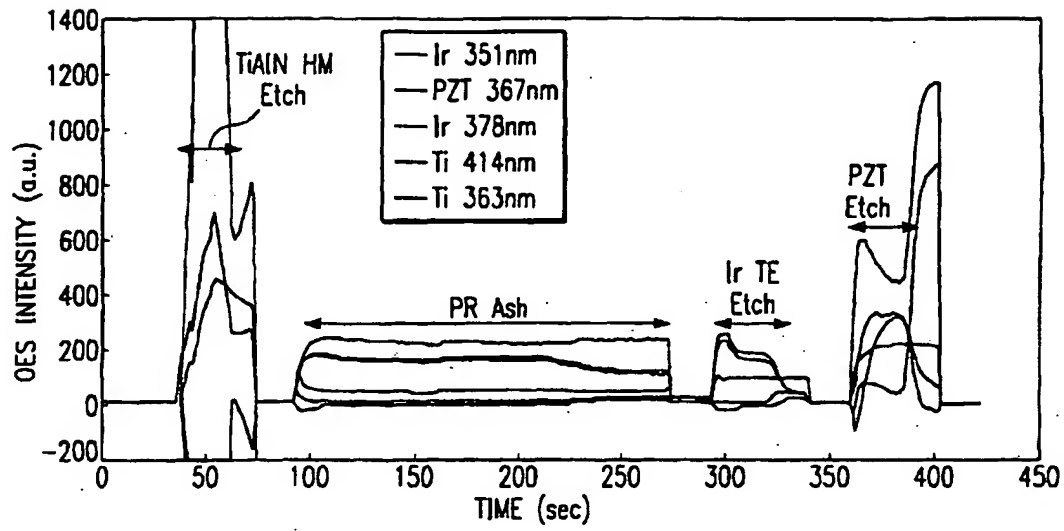


FIG. 9e

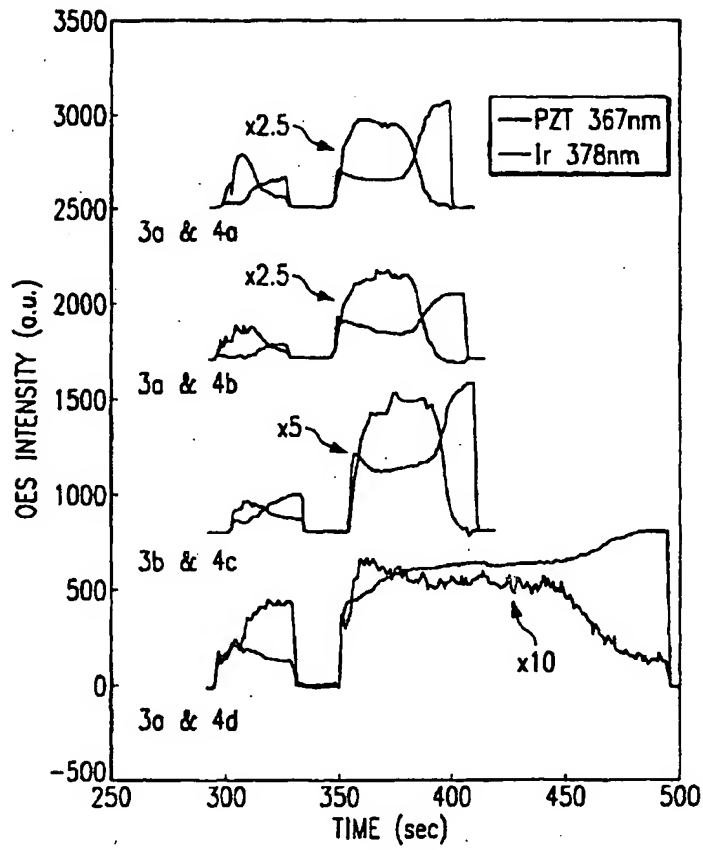


FIG. 9f

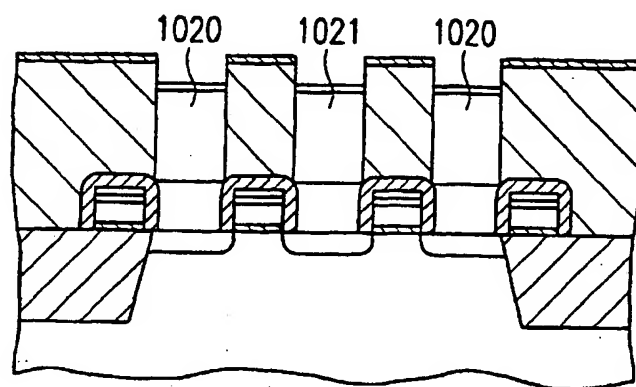


FIG. 10a

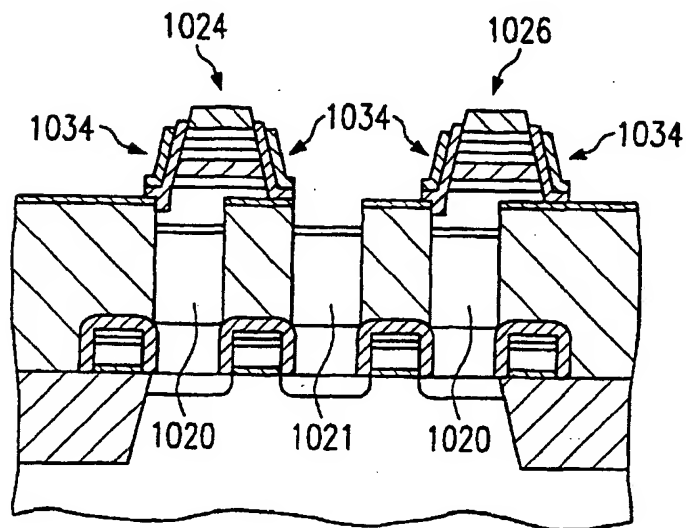


FIG. 10b

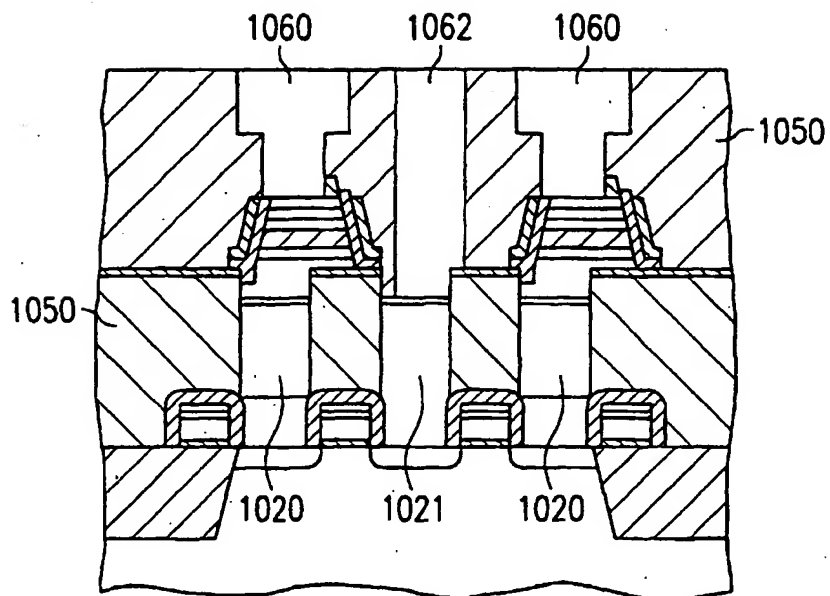


FIG. 10c

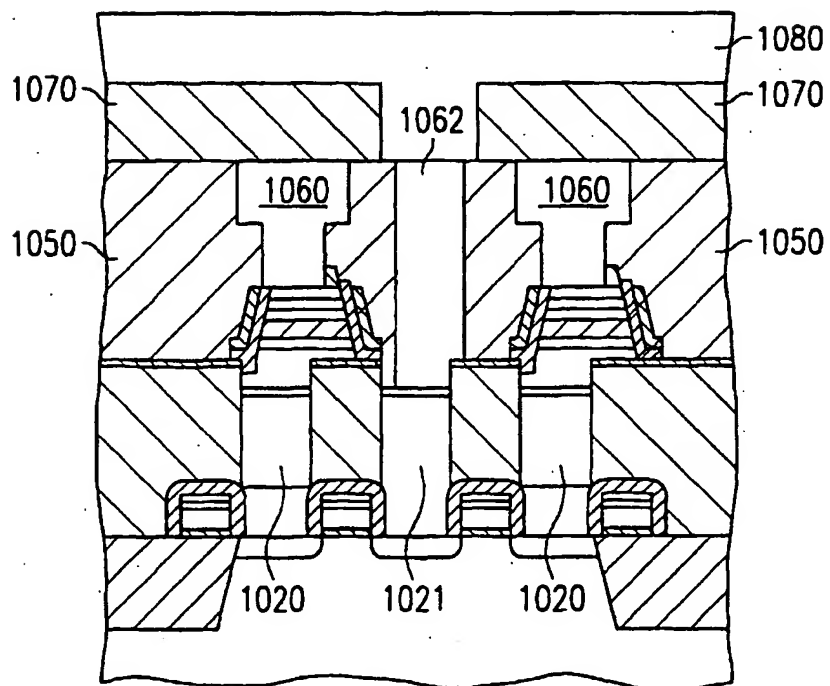


FIG. 10d

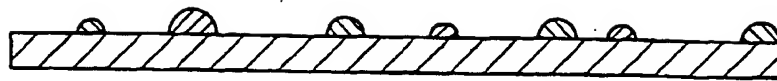


FIG. 11a

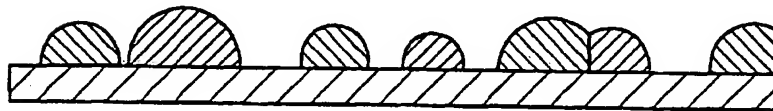


FIG. 11b

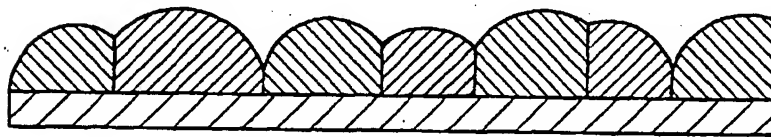


FIG. 11c

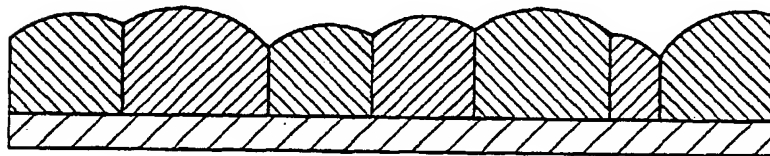


FIG. 11d

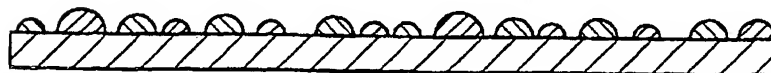


FIG. 11e

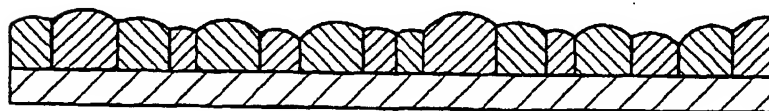


FIG. 11f

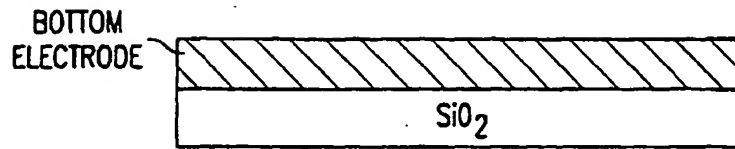


FIG. 12a

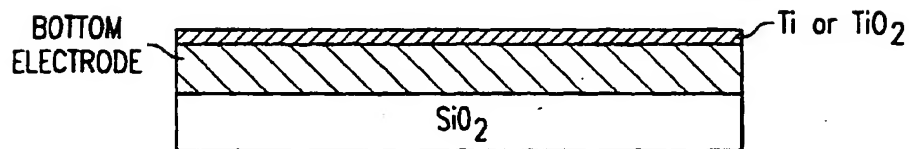


FIG. 12b

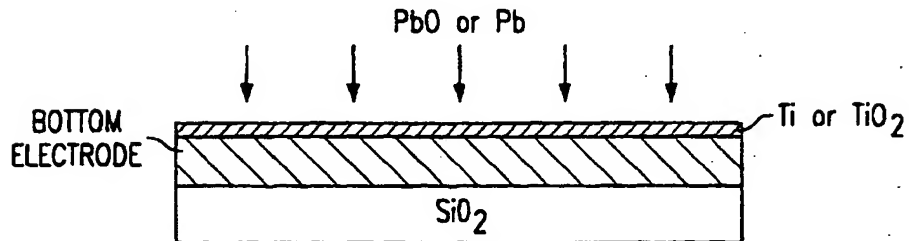


FIG. 12c

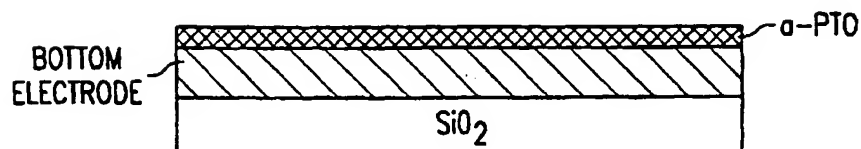


FIG. 12d

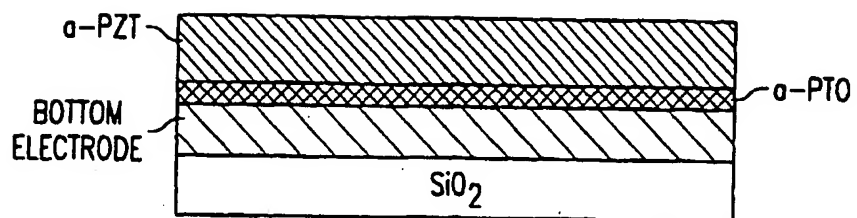


FIG. 12e

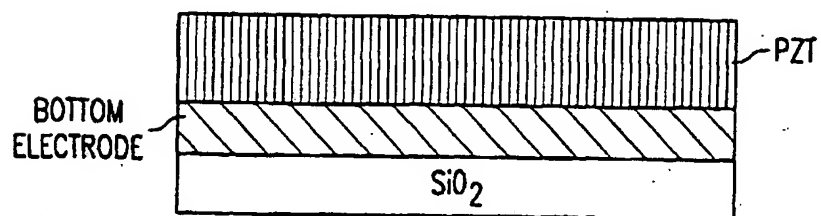


FIG. 12f

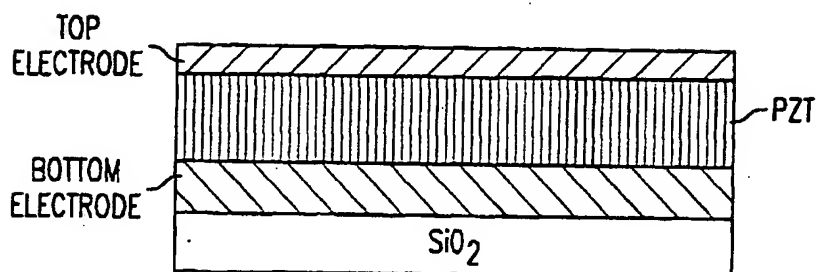


FIG. 12g

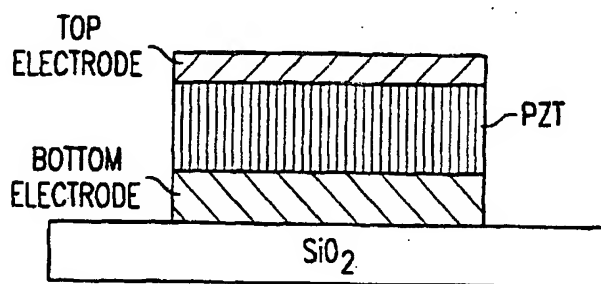


FIG. 12h

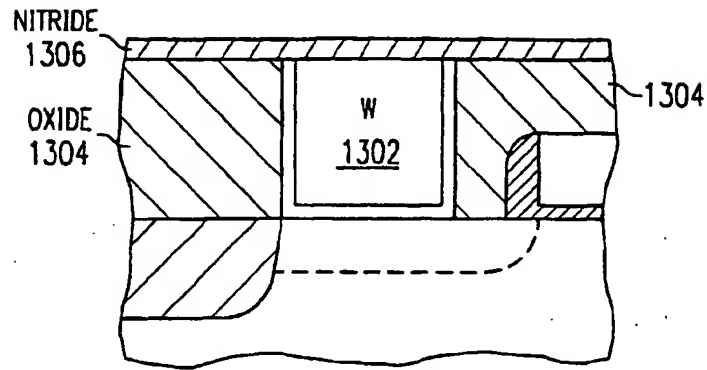


FIG. 13a

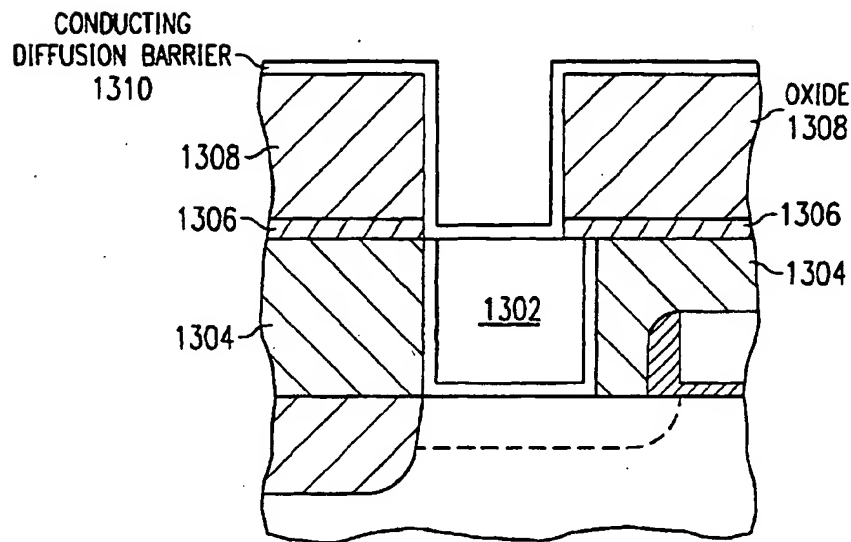


FIG. 13b

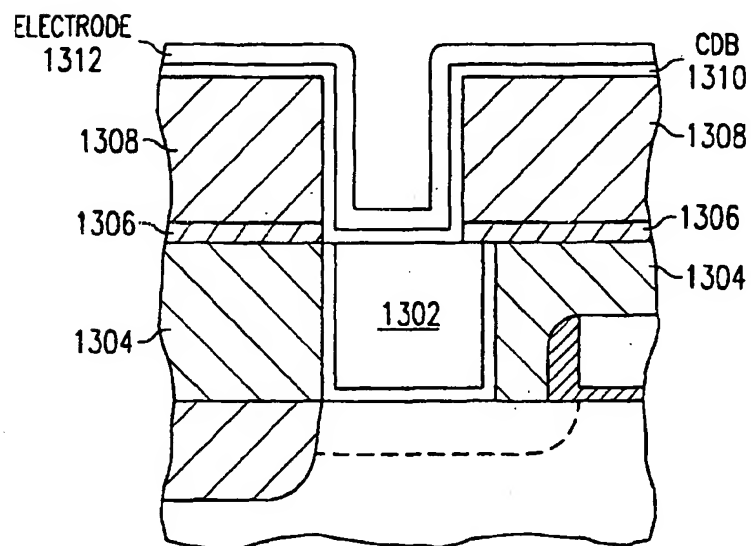


FIG. 13c

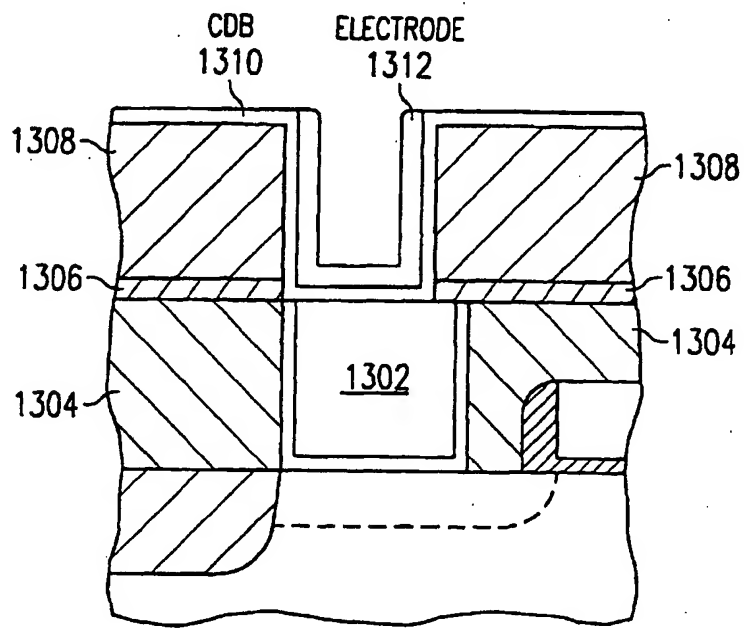


FIG. 13d

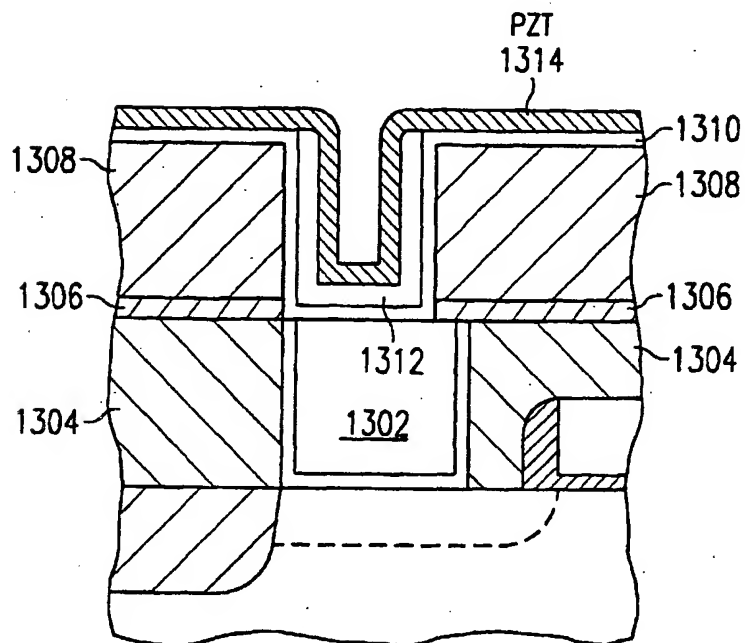


FIG. 13e

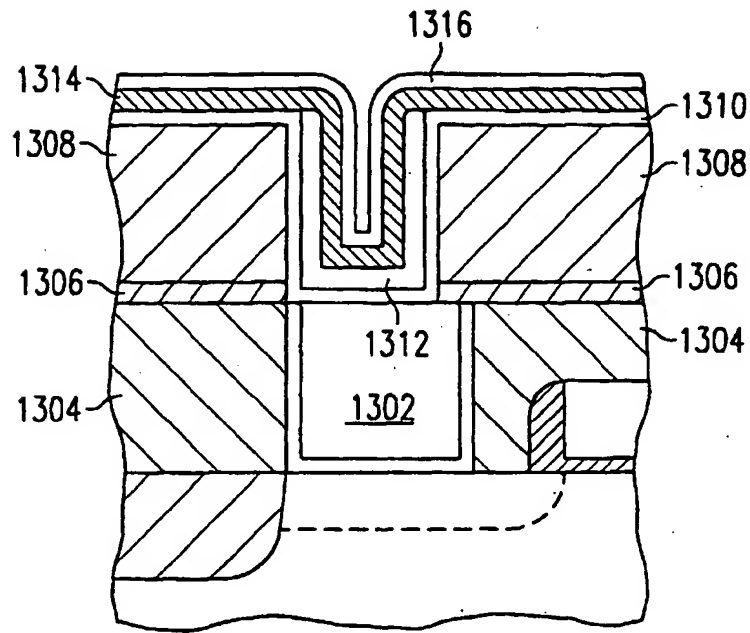


FIG. 13f

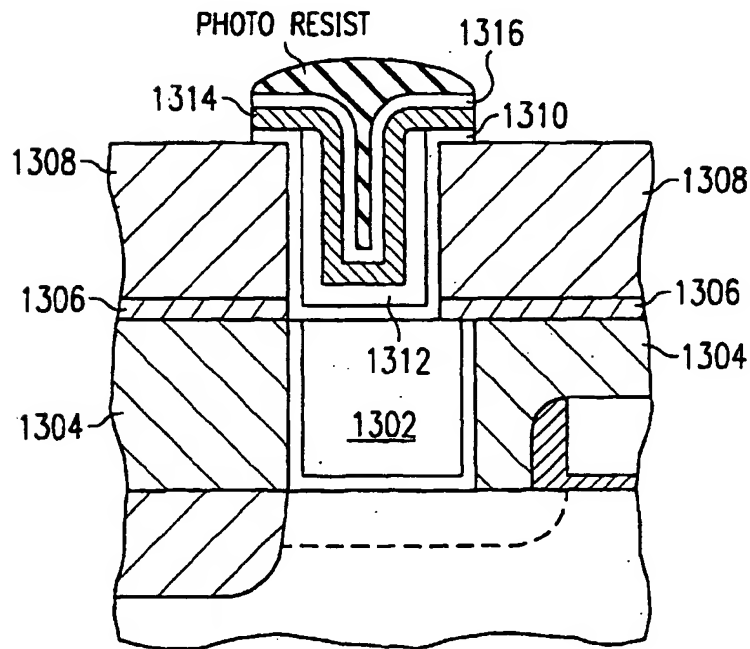


FIG. 13g

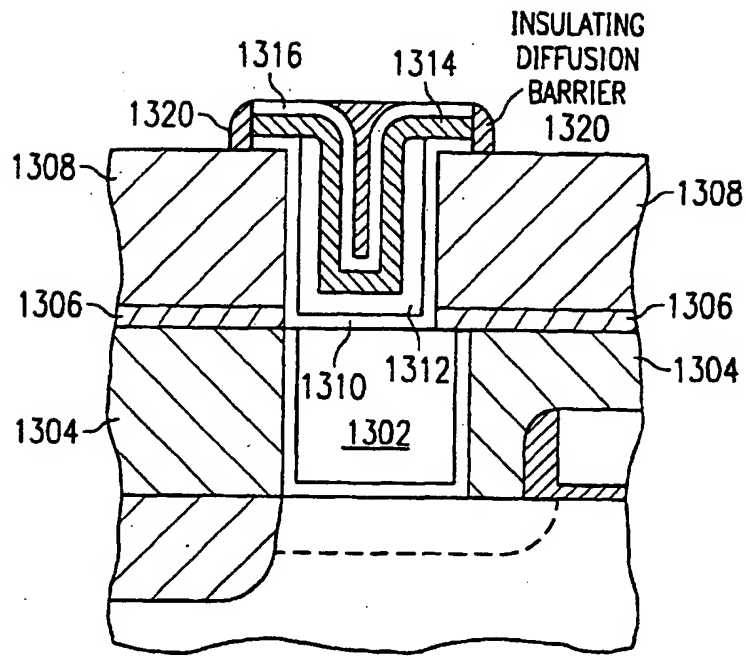


FIG. 13h

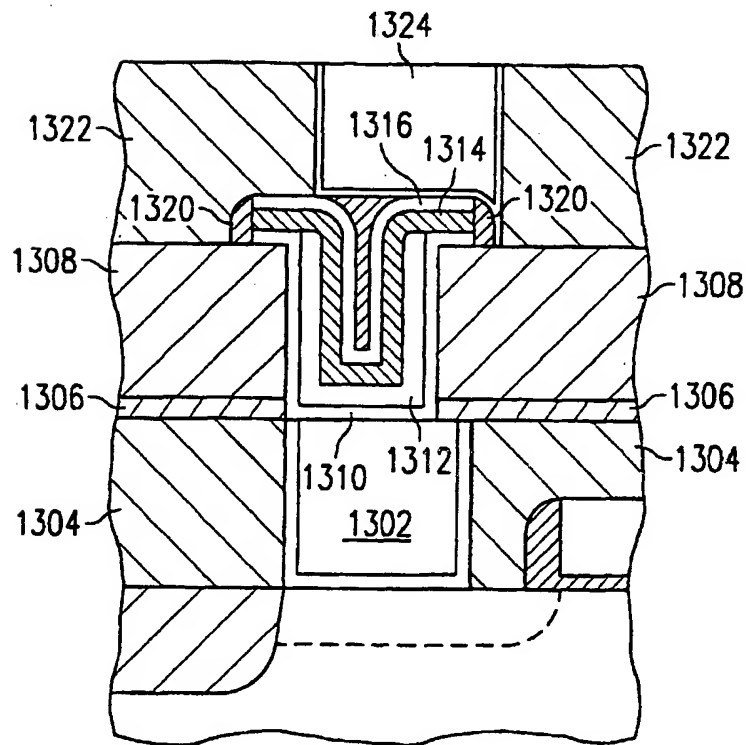


FIG. 13i

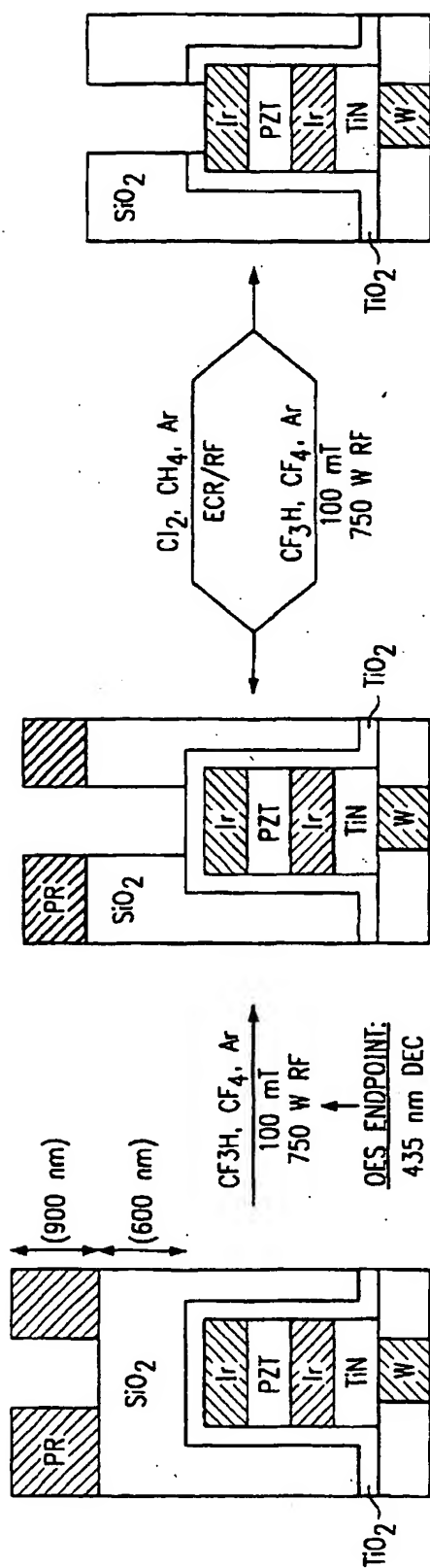


FIG. 14

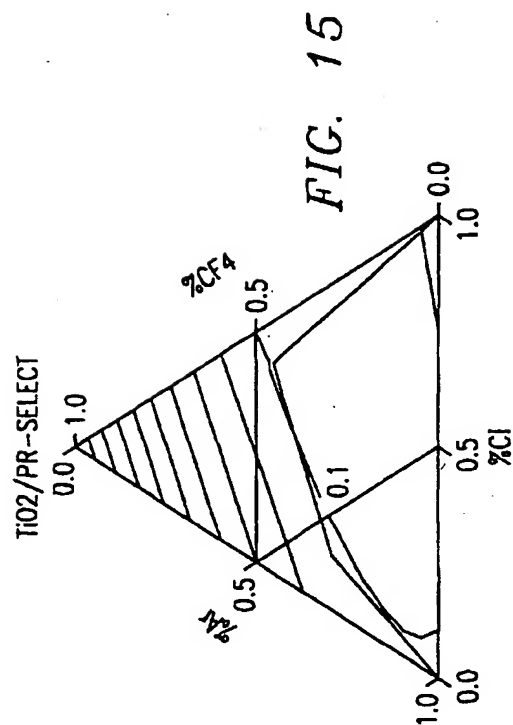


FIG. 15



(11) **EP 1 001 459 A3**

(12) **EUROPEAN PATENT APPLICATION**

(88) Date of publication A3:
 20.09.2000 Bulletin 2000/38

(51) Int. Cl.⁷: **H01L 21/311**, H01L 21/02,
 H01L 21/8242, H01L 29/51,
 H01L 27/108

(43) Date of publication A2:
 17.05.2000 Bulletin 2000/20

(21) Application number: 99202911.6

(22) Date of filing: 09.09.1999

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
 Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 09.09.1998 US 99571 P
 11.09.1998 US 99848 P
 30.12.1998 US 114228 P
 10.03.1999 US 123687 P

(71) Applicant:
Texas Instruments Incorporated
Dallas, Texas 75251 (US)

(72) Inventors:
 • **Moise, Theodore S.**
Dallas, Texas 75238 (US)
 • **Xing, Guoqiang**
Plano, Texas 75093 (US)

- **Visokay, Mark**
Bolse ID 83716 (US)
- **Gaynor, Justin F.**
Dallas, Texas 75214 (US)
- **Summerfelt, Scott R.**
Garland, Texas 75094 (US)
- **Gilbert, Stephen R.**
Dallas, Texas 75204 (US)
- **Celii, Francis**
Dallas, Texas 75248 (US)
- **Colombo, Luigi**
Dallas, Texas 75248 (US)
- **Kressley, Mark A.**
Richardson, Texas 75081 (US)

(74) Representative: **Holt, Michael**
Texas Instruments Limited,
European Patents Department (MS 13),
PO Box 5069
Northampton NN4 7ZE (GB)

(54) **Integrated circuit comprising a capacitor and method**

(57) A via etch to contact a capacitor with ferroelectric between electrodes together with dielectric on an insulating diffusion barrier includes two-step etch with F-based dielectric etch and Cl- and F-based barrier etch.

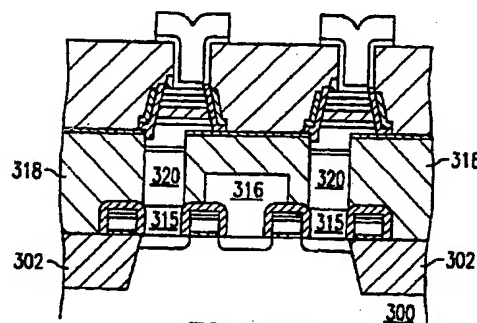


FIG. 6f

EP 1 001 459 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 20 2911

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	EP 0 786 805 A (MATSUSHITA ELECTRONICS CORP) 30 July 1997 (1997-07-30) * figures 1-4 * * column 3, line 7 - column 7, line 43 *	4,6	H01L21/311 H01L21/02 H01L21/8242 H01L29/51 H01L27/108
A	---	1-3,5	
X	EP 0 557 937 A (RAMTRON INT CORP) 1 September 1993 (1993-09-01) * figures 1-12 * * column 3, line 26 - column 7, line 25 *	6	
A	---	3-5	
X	US 5 554 866 A (BHATTACHARYA PIJUSH ET AL) 10 September 1996 (1996-09-10) * figures 1-8 * * column 5, line 49 - column 7, line 17 *	6	
A	---	1-5	
Y	EP 0 823 726 A (SIEMENS AG) 11 February 1998 (1998-02-11) * column 4, line 34 - line 47 * * column 4, line 56 - column 5, line 33 *	1	
A	---	3,6	
Y	KHAMANKAR R B ET AL: "A NOVEL BST STORAGE CAPACITOR NODE TECHNOLOGY USING PLATINUM ELECTRODES FOR GBIT DRAMS" INTERNATIONAL ELECTRON DEVICES MEETING, US, NEW YORK, NY: IEEE, 1997, pages 245-248, XP000855788 ISBN: 0-7803-4101-5 * paragraphs 'CAPACITOR...!', 'PT...!' * * figures 1A, 2, 9 *	1	
A	---	2,3	
	---	-/--	
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 19 July 2000	Examiner Polesello, P
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03/82 (P04C01)



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 20 2911

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
P,X	DE 197 28 473 A (SIEMENS AG) 7 January 1999 (1999-01-07) * figures 1-5 * * column 2, line 59 - column 3, line 65 * * column 4, line 4 - line 61 * * claim 9 *	1	
P,A	----	2-4,6	
A	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 08, 30 June 1998 (1998-06-30) -& JP 10 064843 A (SAMSUNG ELECTRON CO. LTD), 6 March 1998 (1998-03-06) * abstract, paragraphs 9-27 *	1,2,6	
A	EP 0 858 103-A (SAMSUNG ELECTRONICS CO LTD) 12 August 1998 (1998-08-12) * figures 1-5 * * column 3, line 21 - column 5, line 37 *	1,2	
A	US 5 705 428 A (LIU LIANJUN ET AL) 6 January 1998 (1998-01-06) * figures 3-6 * * column 2, line 11 - line 37 * * column 3, line 20 - column 4, line 14 *	1,2	
A	US 5 780 315 A (CHAO YING-CHEN ET AL) 14 July 1998 (1998-07-14) * figures 1,2 * * column 4, line 13 - column 5, line 19 *	3	
A	PATENT ABSTRACTS OF JAPAN vol. 1996, no. 11, 29 November 1996 (1996-11-29) -& JP 08 186120 A (NEC CORP), 16 July 1996 (1996-07-16) * abstract, paragraphs 12-33; figures 1-3 * ----- -/--	1	
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 19 July 2000	Examiner Polesello, P
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03/82 (P04C01)



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 20 2911

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	PATENT ABSTRACTS OF JAPAN vol. 014, no. 190 (E-0918), 18 April 1990 (1990-04-18) -& JP 02 039433 A (NEC CORP), 8 February 1990 (1990-02-08) * abstract; figure 1 *	1	
A	US 5 607 602 A (GOTO HARUHIRO ET AL) 4 March 1997 (1997-03-04) * column 4, line 15 - line 50 *	3	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 19 July 2000	Examiner Polesello, P
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03.82 (P4/C01)



European Patent
Office

Application Number

EP 99 20 2911

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

- ☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
- ☐ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:



European Patent
Office

LACK OF UNITY OF INVENTION
SHEET B

Application Number
EP 99 20 2911

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. Claims: 1,2

Method of plasma etching a material using a Ti/Al nitride hardmask.

2. Claims: 3-5

Method of forming a ferroelectric capacitor with a bottom and a top diffusion barriers consisting of plasma etching a stack of these materials.

3. Claim : 6

Method of forming a capacitor where the bottom electrode is surface oxidized before dielectric deposition.

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

19-07-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0786805 A	30-07-1997	JP 9266200 A	07-10-1997
		US 5840200 A	24-11-1998
EP 0557937 A	01-09-1993	JP 6013565 A	21-01-1994
		US 5374578 A	20-12-1994
US 5554866 A	10-09-1996	US 5554564 A	10-09-1996
		EP 0697718 A	21-02-1996
		US 5811851 A	22-09-1998
EP 0823726 A	11-02-1998	DE 19631622 A	12-02-1998
		JP 10088373 A	07-04-1998
DE 19728473 A	07-01-1999	NONE	
JP 10064843 A	06-03-1998	NONE	
EP 0858103 A	12-08-1998	CN 1190251 A	12-08-1998
		JP 10223604 A	21-08-1998
		US 6004882 A	21-12-1999
US 5705428 A	06-01-1998	SG 52811 A	28-09-1998
US 5780315 A	14-07-1998	NONE	
JP 08186120 A	16-07-1996	NONE	
JP 02039433 A	08-02-1990	NONE	
US 5607602 A	04-03-1997	JP 2875208 B	31-03-1999
		JP 9120967 A	06-05-1997
		JP 11219941 A	10-08-1999

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82